U.S. DEPARTMENT OF COMMERCE
National Technical Information Service

PB-281 489

Industrial Process Profiles for Environmental Use: Chapter 22. The Phosphate Rock and Basic Fertilizer Materials Industry

Radian Corp, Austin, Tex.

Prepared for

Industrial Environmental Research Lab.-Cincinnati, Ohio

Feb 77

PB 281 489

EPA-600/2-77-023v
February 1977

Environmental Protection Technology Series

INDUSTRIAL PROCESS PROFILES FOR ENVIRONMENTAL USE: Chapter 22. The Phosphate Rock and Basic Fertilizer Materials Industry

Industrial Environmental Research Laboratory
Office of Research and Development
U.S. Environmental Protection Agency
Cincinnati, Ohio 45268

REPRODUCED BY
NATIONAL TECHNICAL
INFORMATION SERVICE
U. S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161

RESEARCH REPORTING SERIES

Research reports of the Office of Research and Development, U.S. Environmental Protection Agency, have been grouped into five series. These five broad categories were established to facilitate further development and application of environmental technology. Elimination of traditional grouping was consciously planned to foster technology transfer and a maximum interface in related fields. The five series are:

1. Environmental Health Effects Research
2. Environmental Protection Technology
3. Ecological Research
4. Environmental Monitoring
5. Socioeconomic Environmental Studies

This report has been assigned to the ENVIRONMENTAL PROTECTION TECHNOLOGY series. This series describes research performed to develop and demonstrate instrumentation, equipment, and methodology to repair or prevent environmental degradation from point and non-point sources of pollution. This work provides the new or improved technology required for the control and treatment of pollution sources to meet environmental quality standards.

This document is available to the public through the National Technical Information Service, Springfield, Virginia 22161.

TECHNICAL REPORT DATA

(Please read Instructions on the reverse before completing)

1. REPORT NO. EPA-600/2-77-023v	2.	3. RECIPIENT'S ACCESSION NO. PB281489
4. TITLE AND SUBTITLE Industrial Process Profiles for Environmental Use: Chapter 22. The Phosphate Rock and Basic Fertilizers Industry		5. REPORT DATE February 1977
		6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) P.E.Muehlberg, J.T.Reding, & B.P.Shepherd (Dow Chem.) Terry Parsons & Glynda E. Wilkins, Editors		8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS Radian Corporation 8500 Shoal Creek Blvd., P.O. Box 9948 Austin, Texas 78766		10. PROGRAM ELEMENT NO. 1AB015
		11. CONTRACT/GRANT NO. 68-02-1319/Task 34
12. SPONSORING AGENCY NAME AND ADDRESS Industrial Environmental Research Laboratory Office of Research and Development U.S. ENVIRONMENTAL PROTECTION AGENCY Cincinnati, Ohio 45268		13. TYPE OF REPORT AND PERIOD COVERED Initial: 8/75-11/76
		14. SPONSORING AGENCY CODE EPA/600/12

15. SUPPLEMENTARY NOTES

16. ABSTRACT

The catalog was developed to aid in defining the environmental impacts of U.S. industrial activity. The phosphate rock and basic fertilizer materials industry produces primarily large-tonnage quantities of both finished fertilizers and basic intermediates for fertilizers. The industry includes companies and processes that produce end products derived from phosphate rock having uses other than as fertilizers. The industry is discussed in eight operations: phosphate rock processing; ammonia synthesis; production of ammonia sulfate, amonium nitrate, and urea; production of potassium nitrate and liquid chlorine; production of ammonium phosphate and nitric phosphate; production of mixed fertilizers; production of elemental phosphorus and furnace acid; and production of sodium phosphates and calcium phosphates. One segment of the industry is distinguished as, and entitled, 'Elemental Phosphorus and Furnace Acid Segment.' One chemical tree, eight process flow sheets, and 45 process descriptions characterize the industry. For each process description, available data is presented on input materials, operating parameters, utility requirements, and waste streams. Related information, provided as appendices, includes company, product and raw material data.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Pollution	Process Assessment	13B
Industrial Processes	Environmental Impact	13H
Chemical Engineering	Basic Fertilizer	07A
Phosphate Deposits	Materials	08G
Fertilizers		02A

18. DISTRIBUTION STATEMENT Release to Public	19. SECURITY CLASS *(This Report)* Unclassified	21. NO. OF PAGES 212
	20. SECURITY CLASS *(This page)* Unclassified	22. PRICE PC A10 MF A01

EPA Form 2220-1 (9-73)

EPA-600/2-77-023v
February 1977

INDUSTRIAL PROCESS PROFILES
FOR ENVIRONMENTAL USE
CHAPTER 22
THE PHOSPHATE ROCK AND BASIC FERTILIZERS INDUSTRY

by

P. E. Muehlberg, J. T. Reding, and B. P. Shepherd
Dow Chemical
Freeport, Texas 77541

Terry Parsons and Glynda E. Wilkins
Radian Corporation
Austin, Texas 78766

Contract No. 68-02-1319

Project Officer
Alfred B. Craig
Metals and Inorganic Chemicals Branch
Industrial Environmental Research Laboratory
Cincinnati, Ohio 45268

INDUSTRIAL ENVIRONMENTAL RESEARCH LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
CINCINNATI, OHIO 45268

DISCLAIMER

This report has been reviewed by the Industrial Environmental Research Laboratory - Cincinnati, U.S. Environmental Protection Agency, and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the U.S. Environmental Protection Agency, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

TABLE OF CONTENTS

CHAPTER 22

Page

INDUSTRY DESCRIPTION.. 1

Raw Materials.. 3

Products.. 4

Companies.. 4

Environmental Impact.. 5

Bibliography.. 6

INDUSTRY ANALYSIS.. 7

PROCESS DESCRIPTIONS.. 8

Phosphate Rock Processing.. 10

Process No. 1. Mining.. 12

Process No. 2. Beneficiation.. 14

Process No. 3. Crushing/Grinding/Screening.. 16

Process No. 4. NSP Process.. 19

Process No. 5. Wet Acid Process.. 21

Process No. 6. TSP Process.. 24

Process No. 7. Sulfuric Acid Manufacture.. 26

Process No. 8. Phosphate Rock Calcination.. 28

Ammonia Synthesis.. 29

Process No. 9. Air Separation.. 31

Process No. 10. Ammonia Feedstock Purification.. 33

Process No. 11. Hydrogen Purification.. 35

Process No. 12. Cryogenic Purification.. 36

Process No. 13. Partial Oxidation.. 38

Process No. 14. Steam Reforming.. 41

Process No. 15. Hydrogen Combustion.. 44

Process No. 16. Ammonia Synthesis.. 45

Production of Ammonium Sulfate, Ammonium Nitrate and Urea........ 47

Process No. 17. HNO_3 Formation.. 49

Process No. 18. NH_4NO_3 Formation.. 52

TABLE OF CONTENTS (Continued)

Page

Process No. 19. Urea Formation.............................. 55
Process No. 20. Urea Finishing.............................. 57
Process No. 21. Ammonium Sulfate Formation.................. 59
Production of Potassium Nitrate and Liquid Chlorine............ 61
Process No. 22. KCL-HNO_3 Reaction........................ 63
Process No. 23. Crystallization/Stripping/Fractionation..... 65
Process No. 24. KNO_3 Drying.............................. 67
Process No. 25. N_2O_4-Cl_2 Fractionation............... 68
Process No. 26. HNO_3 Formation/Absorption................ 70
Production of Ammonium Phosphates and Nitric Phosphate......... 71
Process No. 27. Neutralization/Granulation/Drying........... 73
Process No. 28. Digestion/Granulation/Drying................ 75
Production of Mixed Fertilizers................................ 77
Process No. 29. Dissolution................................. 79
Process No. 30. Ammoniation/Granulation/Drying.............. 81
Process No. 31. Dissolution/Slurrying....................... 83
Process No. 32. Bulk Blending............................... 85
Elemental Phosphorus and Furnace Acid Segment.................. 87
Production of Elemental Phosphorus and Furnace Acid............ 88
Process No. 33. Furnace Charge Preparation.................. 90
Process No. 34. Electric Furnace Process.................... 92
Process No. 35. Off-Gas Combustion.......................... 94
Process No. 36. Phosphorus Recovery......................... 96
Process No. 37. Phosphorus Combustion....................... 98
Process No. 38. P_2O_5 Recovery........................... 100
Process No. 39. Absorption/Purification..................... 101
Production of Sodium Phosphates and Calcium Phosphates......... 103
Process No. 40. Neutralization/Filtration................... 105
Process No. 41. Crystallization/Drying...................... 107
Process No. 42. Calcination................................. 109
Process No. 43. Fusion...................................... 111
Process No. 44. CaO-H_3PO_4 Reaction...................... 112
Process No. 45. Calcium Phosphate Drying.................... 114

TABLE OF CONTENTS (Continued)

Page

APPENDIX A - Raw Materials 115

APPENDIX B - Product List. 121

APPENDIX C - Company/Product Lists 125

APPENDIX D - Fertilizer Industry Bibliography. 187

Directory, Fertilizer Plants in the United States

LIST OF FIGURES

CHAPTER 22

Figure		Page
1	Chemical Tree - Phosphate Rock and Basic Fertilizer Materials Industry	9
2	Phosphate Rock Processing	11
3	Ammonia Synthesis	30
4	Ammonium Sulfate, Ammonium Nitrate and Urea	48
5	Potassium Nitrate and Liquid Chlorine	62
6	Ammonium Phosphates and Nitric Phosphate	72
7	Mixed Fertilizers	78
8	Elemental Phosphorus and Furnace Acid	89
9	Sodium Phosphates and Calcium Phosphates	104

LIST OF TABLES

CHAPTER 22

Table		Page
A-1	Representative Analyses of Commercial Phosphate Rocks.	119
C-1	Producers of Ammonia (Anhydrous and Aqua).	126
C-2	Producers of Ammonium Nitrate.	131
C-3	Producers of Ammonium Phosphates	134
C-4	Producers of Ammonium Sulfate.	137
C-5	Producers of Bulk-Blended Mixed Fertilizers.	138
C-6	Producers of Calcium Phosphates.	139
C-7	Producers of Chlorine, Liquid.	141
C-8	Producers of Defluorinated Phosphate Rock.	142
C-9	Producers of Ferrophosphorous.	143
C-10	Producers of Fluorosilicic (Hydrofluosilicic Acid) . .	144
C-11	Producers of Granular Mixed Fertilizers	146
C-12	Producers of Gypsum	147
C-13	Producers of Liquid Mixed Fertilizers.	148
C-14	Producers of Liquid Suspensions.	149
C-15	Producers of Marketable Phosphate Rock	150
C-16	Producers of Nitric Acid	153
C-17	Producers of Nitric Phosphate.	158
C-18	Producers of Phosphoric Acids, Ortho	159
C-19	Producers of Phosphoric Acids, Super	163
C-20	Producers of Phosphorous, Elemental.	165

LIST OF TABLES (Continued)

Table		Page
C-21	Producers of Phosphorous, Pentoxide	166
C-22	Producers of Potassium Nitrate.	167
C-23	Producers of Slag	168
C-24	Producers of Sodium Orthophosphates and Polyphosphates	169
C-25	Producers of Sulfuric Acid.	174
C-26	Producers of Superphosphate, Normal	181
C-27	Producers of Superphosphate, Triple	183
C-28	Producers of Urea	184

ACKNOWLEDGEMENTS

This catalog entry was prepared for EPA by Dow Chemical U.S.A., Texas Division, Freeport, Texas, under Contract No. 68-02-1329, Task 8. P. E. Muehlberg, J. T. Reding and B. P. Shepherd were the authors of this report.

Helpful review comments from Denzel A. Brown were received and incorporated into this chapter.

PHOSPHATE ROCK AND BASIC FERTILIZER MATERIALS INDUSTRY

INDUSTRY DESCRIPTION

The companies populating the industry produce primarily large-tonnage quantities of both finished fertilizers and the basic intermediates for fertilizers. Companies and processes which produce end products derived from phosphate rock having uses other than as fertilizers are included in the industry. Historically, most non-fertilizer production occurs in an industry segment that is distinguished by a group of products which are derived from the electric furnace process for the production of elemental phosphorous: Included are furnace acid and the inorganic phosphates produced from furnace acid. This segment has been entitled "Elemental Phosphorous and Furnace Acid Segment" and is described in further detail in a separate segment description.

Primary raw materials used by the industry are:

- phosphate rock
- nitrogen from air
- hydrogen from hydrogen containing materials, especially natural gas
- sulfur

These raw materials are upgraded and combined with secondary raw materials from the potash products industry to produce 30 to 40 end products.

To facilitate description, the 45 processes used by the industry have been divided into eight operations:

1) Phosphate Rock Processing
2) Ammonia Synthesis
3) Production of Ammonium Sulfate, Ammonium Nitrate and Urea
4) Production of Potassium Nitrate and Liquid Chlorine
5) Production of Ammonium Phosphate and Nitric Phosphate
6) Production of Mixed Fertilizers
7) Production of Elemental Phosphorous and Furnace Acid
8) Production of Sodium Phosphates and Calcium Phosphates

Each of these groups of technologically related processes is diagrammed on a separate flowsheet. The processes indicated on a given flowsheet convert a small group of input materials to a group of technologically related end products, intermediate products, by products and/or waste materials. Details concerning the conversion of raw materials to finished products are given under "Industry Analysis" and in individual Process Descriptions.

Industry functions are conducted in an estimated six thousand to seven thousand separate facilities. These facilities are unevenly dispersed throughout forty eight states. More than 97 percent of these installations are blending plants for mixed fertilizers. Their geographic locations follow approximately the distribution pattern of the acreage of cultivated land.

The installations producing the more basic fertilizer intermediates, such as superphosphates, wet-process phosphoric acid, or ammonia, are, for economic reasons situated near phosphate rock mines or near low-cost supplies of hydrocarbons or other hydrogen-containing materials.

The size of a single facility varies from an estimated half-dozen full- or part-time employees working in a mixed-fertilizer bulk-blending plant up to a level of between one thousand and fifteen hundred people employed in an integrated facility mining and processing phosphate rock as well as producing ammonium phosphates and urea from captively produced ammonia. In the former example, the equipment involved might be valued at as little as one or two hundred thousand dollars. The total fixed investment in the latter case may be several hundred million dollars.

Total employment in the industry during 1973 is estimated between fifty and sixty-five thousand persons.

The combined dry-basis weight of all end products leaving the industry during 1974 is estimated to be between 55 and 65 million metric tons. This total net tonnage was produced from approximately 125 million metric tons of crude phosphate rock plus the total hydrocarbon equivalent of more than 1.5 billion cubic meters of natural gas and about seven million metric tons of purchased potash materials. The fertilizer industry consumed approximately 17.6 million metric tons of sulfuric acid during 1974, or about 56 percent of the total U.S. consumption of sulfuric acid for all purposes.

The industry in general has experienced an annual growth rate of slightly greater than 3.5 percent since 1970. Forecasts of its growth rate to 1980 are between three and five percent per year. These rates do not apply to the Elemental Phosphorus and Furnace Acid Segment. The segment has been shrinking since 1970. The decline is predicted to continue in the near future.

It is believed that all industry companies use purchased power. Possible exceptions are milti-industry facilities of some large corporations such as Allied Chemical Corporation or the Monsanto Company, where on-site power may be generated. The phosphorus furnaces of Tennessee Valley Authority, which used TVA-generated power, are now inoperative.

Raw Materials

The large-tonnage primary raw materials of the industry are:

- Phosphate rock deposits, owned by industry companies.
- Air, as the nitrogen source for ammonia.
- Hydrogen-containing materials, such as electrolysis-cell hydrogen, natural gas and naphtha. These may be either captive or purchased.
- Sulfur, as the source of sulfuric acid. This is purchased from outside the industry.
- Other primary raw materials include lime and soda ash.

Secondary raw materials include:

- Potash materials, usually potassium chloride. Normally purchased.
- Sulfuric acid, purchased to augment captive production.
- Iron - for use in the Electric Furnace Process.

Phosphate rock deposits represent by far the largest tonnage of raw material. Deposits occur in three distinct areas:

- Florida-North Carolina, accounting for about 70 percent of current domestic output. This area generally contains the lowest grade rock deposits, but produces the highest grade of beneficiated rock.
- Tennessee, has the smallest output of the three areas and produces the lowest grade of beneficiated rock.
- Western states (Idaho, Montana, Utah, and Wyoming). The grade of the deposits is highest in this area. The rock needs little beneficiation.

More than 95% of the crude phosphate rock produced is mined by open-pit methods. Reclamation of worked-over land and necessity of maintaining sludge ponds for slimes disposal are the two largest continuing environmental problems.

Natural gas and other light hydrocarbons such as naphtha are by far the major source of hydrogen for ammonia production, estimated to account for about 90 percent of the ammonia produced. Electrolysis hydrogen, stripped coke-oven gas, and off-gas from cracking processes account for the remainder. No environmental problems result from transportation or storage of hydrogen feed streams.

Natural gas, potash, and sulfur are materials which are in some instances purchased, and in other cases produced captively by large multi-industry companies. The operations of International Minerals and Chemical Corporation, Lone Star Gas Company, Arkansas Louisiana Gas Company, Texas-gulf, and Freeport Minerals Company are examples of vertically integrated production. In most cases, however, these raw materials are purchased.

Sulfuric acid is the only raw material having any notable toxicity or other potentially harmful properties.

A complete list of industry raw materials is included in Appendix A.

Products

The industry produces 30 to 40 end products. Several of these, such as phosphoric acid, and the phosphates of calcium, sodium and ammonia, include more than one distinct compound.

Four by-products are generated: gypsum, furnace slag, fluorosilicic acid, and liquid chlorine.

The distribution, estimated here, of the approximately sixty million metric tons of end products leaving the industry in 1974 was:

•Domestically consumed end-use fertilizers	- 73%
•Exports, chiefly phosphate rock	- 23%
•Non-fertilizer use	- 4%

The latter category includes:

- Detergents
- Elemental phosphorus for compounds produced by other industries
- Beverages, foods, animal feed additives
- Rust preventatives
- Ferro-phosphorus for the steel industry.

Less than five percent of the by-product gypsum is beneficially used as a soil conditioner and in manufacture of wallboard. Furnace slag is sold for road and railway ballast. Fluorosilicic acid is mainly used in fluoridizing municipal water supplies.

A complete list of products and by-products may be found in Appendix B.

Companies

All of the companies conducting at least one operation in the industry belong to one or the other of three groups:

- Companies (or individuals) who conduct only a blending process to produce a mixed fertilizer material ready for application to the soil. This group numbers between four thousand and six thousand small companies, each employing an estimated three to ten persons. Their processes are dry bulk-blending, granulation, liquid-mixing, and liquid suspension mixing. Frequently, the individual companies are members of cooperatives.

- Companies who produce the intermediate materials for the first group, and who may also themselves produce the identical end-of-the-line products in competition with the first group. About 110 companies are represented in this group. They vary in size from 100 to more than 2000 employees (estimated) and may actually be divisions or subsidiary companies of much larger, multi-industry organizations. Several cooperatives are included. Operations of this group usually produce several basic end-products.

.Companies which use the Electric Furnace Process to manufacture products for non-fertilizer end uses. These companies may also produce intermediate materials for fertilizers or fertilizers.

Approximately seventy five percent of the combined tonnage of end products leaving the industry results from material processed by the eleven companies listed below in the estimated order of decreasing tonnage produced:

International Minerals and Chemical Corporation
The Williams Company (Agrico)
Mobil Oil Company (Mobile Chemical Company)
Monsanto Company (Monsanto Agriculatural Products Company)
Esmark, Incorporated (Swift Chemical Company)
Texasgulf Incorporated
Brewster Phosphates
W. R. Grace & Company
J. R. Simplot Company
Stauffer Chemical Company
United States Steel Corporation (USS Agri-Chemicals)

A more nearly complete list of industry companies is given in Appendix C.

Environmental Impact

Seven environment-related problems continue to be of concern to the industry:

- Reclamation of worked-over land in open-pit mining of phosphate rock.
- Disposal of slimes from wet process beneficiation of phosphate rock. Micron-size slime particles require years to settle in tailings ponds. Pond dikes are subject to breakage. Damages of thirty million dollars are claimed from one such breakage. More than forty-two thousand acres are occupied by slime ponds.
- Disposal of gypsum waste from wet-process acid operations. Waste piles frequently attain heights of 30 meters.
- Fluorine-containing emissions from operations producing superphosphates, wet-process acid, and defluorinated rock.
- NO_x content of tail gases from nitric acid absorbers.
- SO_x content of tail gases from sulfuric acid plants.
- Treatment of "phossy water" discharged from elemental phosphorus recovery in electric furnace operations.

Progress toward satisfactory solutions of these problems has been reported in the literature. The industry has spent more than 100 million dollars to date in these problem areas.

Bibliography

Chemical Economics Handbook, McCaleb, K. E.(ed.). Menlo Park, Stanford Research Institute.

Directory of Fertilizer Manufacturers in the United States, Bulletin Y-87, Hargett, N. (ed.). Muscle Shoals, National Fertilizer Development Center, Tennessee Valley Authority, January 1975.

Hargett, N. Personal communication. July 1975.

Slack, A. V. Fertilizers. In: Kirk-Othmer Encyclopedia of Chemical Technology, 2nd Edition. Standen, A. (ed.). New York, Interscience Publishers, 1966. 9:25-150.

Slack, A. V. Personal communication. July 1975.

Stowasser, W. F. Phosphate Rock. In: Minerals Yearbook, 1972. Shreck, A. E. (ed.). Washington, U. S. Dept. Interior, Bur. Mines, 1974. I:1027-1041.

Stowasser, W. F. Personal communication. July 1975.

Van Wazer, J. R. Phosphorus and the Phosphides. In: Kirk-Othmer Encyclopedia of Chemical Technology, 2nd Edition. Standen, A. (ed.). New York, Interscience Publishers, 1968. 15:291.

Wang, K-L., B. W. Klein and A. F. Powell. Economic Significance of the Florida Phosphate Industry. Washington, U. S. Dept. of Interior, Bur. Mines. 1974. 51 p.

INDUSTRY ANALYSIS

The fertilizer industry is generally competitive and operations are standardized. Data and information on processes are therefore believed to be representative of operating plants. In some instances, information on emissions or utilities is not available.

Figure 1 is a chemical tree which has been included to provide an overview of the material flow for the entire industry.

Figures 2 through 9 present the flow of materials through the 45 processes used in the entire industry. Figures 8 and 9 are devoted to processes used in the Elemental Phosphorous and Furnace Acid Segment of the industry. Each figure is a flowsheet for a group of technically related processes (termed operations) by means of which a few input materials are converted to end-products, intermediate products, by-products and/or waste materials. The flow of intermediate products from one operation to another is indicated by numbered circles keyed to Figure Numbers.

A brief description of input materials and products for each operation precedes its flow sheet. The process descriptions for the processes appearing on the flow sheet follow it.

The interior of each of the rectangular "process blocks" appearing on the flow sheets represents at least one, and usually several, of the sequential, real processes of the operations depicted by the flow sheet. In the ensuing context, the word "process" refers to what occurs inside the process block.

A number and title have been placed within each of the process blocks. These identifying symbols are used in the process descriptions immediately following each figure.

Flag symbols at the upper right-hand corner of the process block indicate the nature of the waste streams, if any, discharged from the process. A circle is used for atmospheric emissions, a triangle for liquid wastes, and a rhombus for solid wastes. The flags do not differentiate between inadvertent (fugitive) and designed wastes.

A verbal process description has been written to characterize each process further, to relate it to other processes, and to quantify its operating parameters. A sample process description format is illustrated following the chemical tree.

Sample Process Description Format

PHOSPHATE ROCK AND BASIC FERTILIZER MATERIALS PROCESS NO. 1

Mining

1. Function - A brief description of Process 1, entitled "Mining," is given here.

2. Input Materials - All materials entering the process are identified here and quantified in metric units per metric ton of the principal end product produced in the operation.

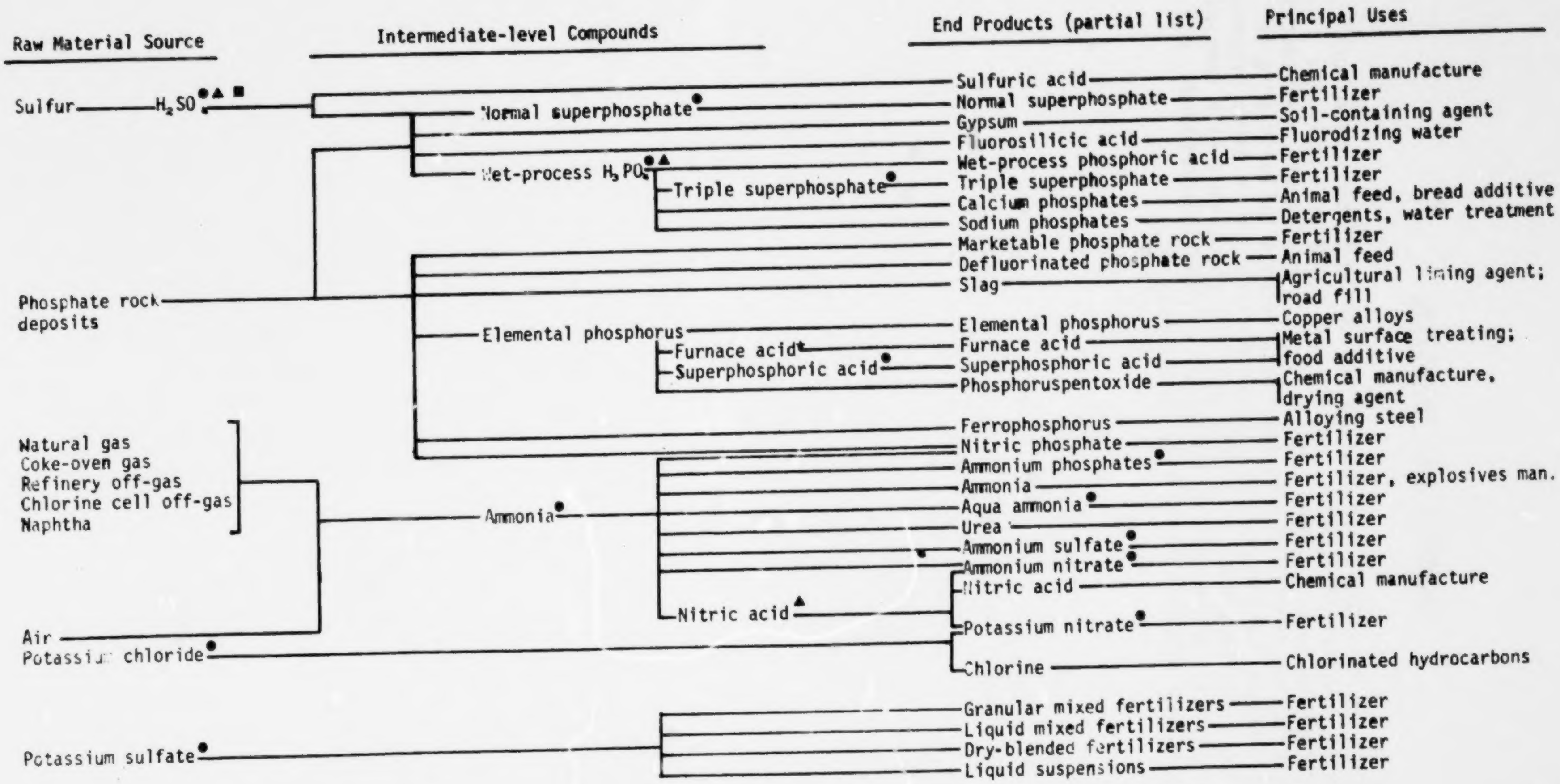
3. Operating Parameters - Listed here is available information on pertinent operating variables and general operating conditions, such as temperature, pressure, flow rates, catalysts, if any, and equipment size.

4. Utilities - Identified and quantified in metric units per metric ton of principal end product.

5. Waste Streams - Liquid wastes, solid wastes, and emissions to the atmosphere are identified here and quantified in metric units per metric ton of principal end products.

6. EPA Source Classification Code - Given here if one exists.

7. References - Information sources are listed here using the format prescribed by the EPA style manual, "Interim Specifications for OR & M Grant, Contract and In-House Reports."


Raw Material Source
Intermediate-level Compounds
End Products (partial list)
Principal Uses
Sulfur
H_2SO_4 ●▲■
Normal superphosphate ●
Wet-process H_3PO_4 ●▲
Triple superphosphate ●
Phosphate rock deposits
Elemental phosphorus
Furnace acid *
Superphosphoric acid ●
Natural gas
Coke-oven gas
Refinery off-gas
Chlorine cell off-gas
Naphtha
Ammonia ●
Nitric acid ▲
Air
Potassium chloride ●
Potassium sulfate ●
Sulfuric acid
Normal superphosphate
Gypsum
Fluorosilicic acid
Wet-process phosphoric acid
Triple superphosphate
Calcium phosphates
Sodium phosphates
Marketable phosphate rock
Defluorinated phosphate rock
Slag
Elemental phosphorus
Furnace acid
Superphosphoric acid
Phosphoruspentoxide
Ferrophosphorus
Nitric phosphate
Ammonium phosphates ●
Ammonia
Aqua ammonia ●
Urea
Ammonium sulfate ●
Ammonium nitrate ●
Nitric acid
Potassium nitrate ●
Chlorine
Granular mixed fertilizers
Liquid mixed fertilizers
Dry-blended fertilizers
Liquid suspensions
Chemical manufacture
Fertilizer
Soil-containing agent
Fluorodizing water
Fertilizer
Fertilizer
Animal feed, bread additive
Detergents, water treatment
Fertilizer
Animal feed
Agricultural liming agent; road fill
Copper alloys
Metal surface treating; food additive
Chemical manufacture, drying agent
Alloying steel
Fertilizer
Fertilizer
Fertilizer, explosives man.
Fertilizer
Fertilizer
Fertilizer
Fertilizer
Chemical manufacture
Fertilizer
Chlorinated hydrocarbons
Fertilizer
Fertilizer
Fertilizer
Fertilizer

- ● Inputs to granular mixed fertilizers, liquid mixed fertilizers, dry blended fertilizers, or liquid suspension fertilizers.
- ▲ Inputs to ammonium phosphates and nitric phosphate products.
- ■ Input to ammonium sulfate.
- * Furnace acid can be used in all places where wet process acid is used.

Figure 1. CHEMICAL TREE - PHOSPHATE ROCK AND BASIC FERTILIZER MATERIALS INDUSTRY

PHOSPHATE ROCK PROCESSING

The processes in this operation include the mining of phosphate rock and its conversion to super phosphates, wet process phosphoric acid and defluorinated phosphate rock. Gypsum and fluorosilicic acid are by-products. Sulfuric acid production from sulfur is described because sulfuric acid is used in the wet process for phosphoric acid manufacture and in other processes in this operation. Environmentally-related problems associated with open-pit mining, slimes disposal, waste gypsum, emissions of fluorine compounds, and sulfur oxide emissions are associated with this operation.

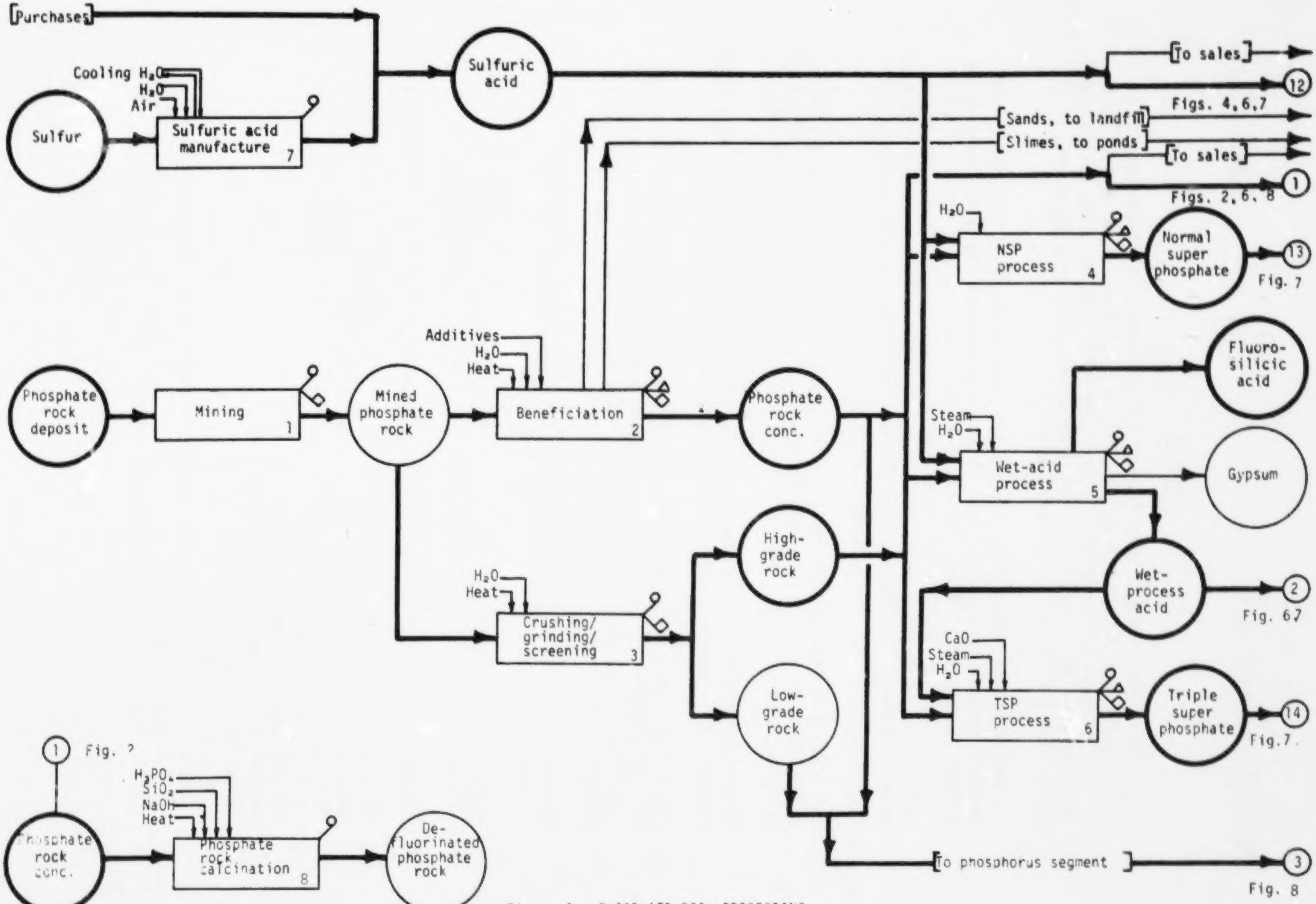

Purchases
Cooling H₂O
H₂O
Air
Sulfur
Sulfuric acid manufacture 7
Sulfuric acid
To sales
12
Figs. 4, 6, 7
Sands, to landfill
Slimes, to ponds
To sales
1
Figs. 2, 6, 8
H₂O
NSP process 4
Normal super phosphate
13
Fig. 7
Additives
H₂O
Heat
Phosphate rock deposit
Mining 1
Mined phosphate rock
Beneficiation 2
Phosphate rock conc.
Fluoro-silicic acid
Steam
H₂O
Wet-acid process 5
Gypsum
H₂O
Heat
Crushing/grinding/screening 3
High-grade rock
Wet-process acid
2
Fig. 67
CaO
Steam
H₂O
TSP process 6
Low-grade rock
Triple super phosphate
14
Fig. 7.
1
Fig. 2
H₃PO₄
SiO₂
NaOH
Heat
Phosphate rock conc.
Phosphate rock calcination 8
De-fluorinated phosphate rock
To phosphorus segment
3
Fig. 8

Figure 2. PHOSPHATE ROCK PROCESSING

Mining

1. Function - The process (See Figure 2) recovers phosphate rock ore (phosphate rock matrix) from subsurface deposits of phosphate rock. Mining methods employed are of the open-pit type in most (estimated greater than 95 percent) of the operations, but include several underground mines in Idaho and Wyoming.

   In the open-pit operations of Florida and North Carolina, the mined rock is deposited by draglines into an excavated sump, disintegrated hydraulically by streams from high-pressure jets, and conveyed as a slurry to the beneficiation plant (Process 2, Figure 2). In some operations, principally in the Western states, the mined ore needs no beneficiation. In these cases, it is forwarded to the crushing and grinding equipment of Process 3 (Figure 2).

   The open-pit type of mining process is characterized by the enormous quantities of overburden removed and by the large quantities of water used to transport the disintegrated rock to the beneficiation plant.

   Principal essential equipment consists of large, specially constructed, electrically-powered draglines, and large centrifugal pumps.

2. Input Materials - The phosphate rock deposit (matrix) plus the overburden constitute the input materials to the process. The phosphate rock matrix is nodular fluoroapatite $[CaF_2 \cdot 3Ca_3(PO_4)_2]$ together with gangue of blue clay and silica sand.

   Per metric ton of marketable rock-plus-concentrates, typical quantities are:

•Overburden removed:	4 to 6 metric tons
•Phosphate rock matrix recovered:	3 to 4 metric tons

3. Operating Parameters - For a typical open-pit operation in Florida:

   •Average overburden thickness: 7 m.
   •Matrix thickness: 0.5 to 16 m, averaging 5 m.
   •Average P_2O_5 content of matrix: ~14%.
   •Surface area mined per year: ~1 km^2.
   •Overburden removed per year: ~1 x 10^7 m^3.
   •Matrix mined per year: ~6 x 10^6 m^3.
   •Dragline parameters:
      ~30 m^3 bucket.
      2500 total installed kW, supplied from 7200 v, 3-phase line.
      90-m boom length.
      2100 metric tons total machine weight.

- Water pressure at hydraulic nozzles: 15 kg/cm^2.
- Solids concentration in transport slurry: ~35%.

4. Utilities - Per metric ton of marketable rock-plus-concentrates:

- 8 to 20 kWh of electrical energy,
- 6 to 8 m^3 of water total, of which 1 to 2 m^3 is make-up.

5. Waste Streams

Four to 6 metric tons of overburden are removed per marketable ton of rock-plus-concentrates. This is temporarily placed in piles, and ultimately deposited in mined areas.
Atmospheric emissions: Fugitive particulate rock emissions (dust) from dragline operation during dry periods is surmised. No quantitative information is available.

6. EPA Source Classification Code

3-05-019-03	Transfer/Storage
3-05-019-04	Open Storage

7. References

Deputy, R., International Minerals and Chemical Corporation. Private Communication. July 1975.

Faith, W. L., D. B. Keyes, and R. L. Clark. Industrial Chemicals, 3rd Edition. New York, John Wiley & Sons, 1965. p. 605-606.

Shreve, R. N. Chemical Process Industries, 3rd Edition. New York, McGraw-Hill, 1967. p. 265-270.

Stowasser, W. F. Phosphate Rock. In: Minerals Yearbook 1972, Shreck, A. E. (ed.). Washington, U. S. Department of the Interior, Bur. Mines, 1974. I:1027-1041.

Stowasser, W. F. Private Communication. June 1975.

Wang, K-L., B. W. Klein, and A. F. Powell. Economic Significance of the Florida Phosphate Industry, Information Circular 8653. Washington, U. S. Bur. Mines, 1974. 51 p.

Beneficiation

1. Function - The process (See Figure 2) separates and recovers the high-grade portion of phosphate rock from the phosphate rock matrix (phosphate rock plus gangue) received from Process 1. The matrix may be received in the form of relatively dry, large lumps. In this case, the beneficiation process usually includes the following steps and equipment.

   - Wet crushing and grinding in hammermills.
   - Wet size separation in log-washers, vibrating-screens, hydroclones, and Evans hydrosizers.
   - Draining on dewatering screens.
   - Drying in rotary dryers.

   If the matrix is received as a water slurry (majority of cases), the beneficiation process usually includes the following steps and equipment:

   - Wet grinding and sizing in equipment as outlined above.
   - Two-step froth-flotation process.
   - Draining on dewatering screens.
   - Drying in rotary dryers.

   The product of the beneficiation process, usually consisting of several size ranges, may be marketed or in integrated operations may be forwarded to Processes 4, 5, 6, or 8, Figure 2; Process 28, Figure 6; or to Process 33, Figure 8.

2. Input Materials - Mined matrix per metric ton of marketable rock concentrates:

   - In Florida/North Carolina: 3 to 4 metric tons, received in form of 30 to 40% slurry.
   - In Tennessee: 1.6 to 1.9 metric tons.
   - In Western states: 1.2 to 1.3 metric tons.

3. Operating Parameters - All process steps are conducted at atmospheric pressure and ambient temperatures.

   Usual size ranges of the three fractions of concentrates produced in Florida:

   - 14-mesh to 18 mm (land pebble)
   - 35-mesh to 14-mesh
   - 150-mesh to 35-mesh

Average P_2O_5 content of composite marketable phosphate rock products:

- Florida-North Carolina: 32.2%
- Tennessee: 26.1%
- Western states: 28.4%

Flotation agents and conditioning additives are used in both stages of froth flotation steps. They are usually amines and tall oil.

Product is dried to approximately 1% residual moisture.

4. Utilities - Based on one metric ton of composite marketable phosphate rock products:

   - Water: 30 m^3, of which 5 m^3 is make-up.
   - Electrical energy: estimated at 20 to 30 kWh.
   - Fuel Oil (for dryers): 4 to 6 kg.

5. Waste Streams - Based on one metric ton of composite marketable phosphate rock products:

   - Sands: Varies from ~0.1 metric ton in Western states operations to ~1.0 metric ton in Florida. These are 14- to 150-mesh size and are used for filling mined-out areas and for dike construction.

   - Slimes: ~1.0 metric ton (dry-basis), consisting of micron-size clay particles suspended in a slurry of ~5% concentration. Approximately 80% of water is reclaimed from slurry in settling ponds. Residual, thickened slurry containing ~20% solids is indefinitely ponded and requires up to 15 years to settle.

   - Particulate atmospheric emissions from rotary dryers are surmised. No quantifying information is available.

6. EPA Source Classification Code - None exists.

   3-05-019-01 Drying

7. References

Faith, W. L., D. B. Keyes, and R. L. Clark. Industrial Chemicals, 3rd Edition. New York, John Wiley & Sons, 1965. p. 605-606.

Shreve, R. N. Chemical Process Industries, 3rd Edition. New York, McGraw-Hill, 1967. p. 265-270.

Stowasser, W. F. Phosphate Rock. In: Minerals Yearbook 1972, Shreck, A. E. (ed.). Washington, U. S. Dept. Interior, Bur. Mines, 1974. I:1027-1041.

Stowasser, W. F. Private Communication. June 1975.

Wang, K-L., B. W. Klein, and A. F. Powell. Economic Significance of the Florida Phosphate Industry, Information Circular 8653. Washington, U. S. Bur. Mines, 1974. 51 p.

Crushing, Grinding, Screening

1. Function - The process (See Figure 2) reduces the size of lumps of mined phosphate rock matrix to the size requirement of various downstream processes. Benefication is neither intended nor accomplished. The process is confined chiefly to the phosphate rock operations of the Western states, where the rock deposits are of marketable grade. The process is also applicable to already segregated ores of lower quality than are usually marketable.

   The process is usually operated wet, but may occasionally be operated dry.

   Process steps usually include the following equipment:

   - Roll crusher (usually operated dry)
   - Wet or dry hammer mills
   - Wet or dry shaking screens
   - Dewatering screens
   - Direct-fired rotary dryer

   Product of the process if high grade is either marketed or, if in a multi-product operation, may be forwarded to Process 4, 5, 6, or 8, Figure 2; Process 28, Figure 6; or Process 33, Figure 8.

   If the product grade is lower than usually marketable for superphosphate production, it is transferred only to Process 33.

2. Input Materials - Phosphate rock, as mined: essentially one metric ton per metric ton of marketable grade phosphate rock.

3. Operating Parameters - Process is conducted at atmospheric pressure and ambient temperatures.

   Typical P_2O_5 content of high-grade rock is 28 to 32%.

4. Utilities - Quantities are based on one metric ton marketable rock:

   - Make-up water: <1 m^3 (estimated)
   - Fuel Oil: 4 to 6 kg if wet-ground;
     <2 kg if dry-ground
   - Electrical energy: 10 to 20 kWh (estimated)

5. Waste Streams - Sediments depositing onto bottom of water-reclaiming ponds (surmised, if process is operated wet): <10 kg per metric ton of high-grade rock.

Particulate atmospheric emissions if process is operated dry: no available quantifying information. Estimated at <10 kg per metric ton of high-grade rock.

6. EPA Source Classification Code

3-05-019-01 Drying

7. References

Shreve, R. N. Chemical Process Industries, 3rd Edition. New York, McGraw-Hill, 1967. p. 265-270.

Stowasser, W. F. Phosphate Rock. In: Minerals Yearbook 1972, Shreck, A. E. (ed.). Washington, U. S. Dept. Interior, Bur. Mines, 1974. I:1027-1041.

Stowasser, W. F. Private Communication. June 1975.

Wang, K-L., B. W. Klein, and A. F. Powell. Economic Significance of the Florida Phosphate Industry, Information Circular 8653. Washington, U. S. Bur. Mines, 1974. 51 p.

NSP Process

1. Function - The process (See Figure 2) converts marketable-grade phosphate rock or phosphate rock concentrates into normal superphosphate (NSP) by reaction with sulfuric acid: $CaF_2 \cdot 3Ca_3(PO_4)_2 + 7H_2SO_4 + 3H_2O \rightarrow 3CaH_4(PO_4)_2 \cdot H_2O + 2HF + 7CaSO_4$

   The normal superphosphate produced is then either marketed for direct end use as fertilizer or used in making blended fertilizer in Process 32, Figure 7.

   The process includes the following sequential steps and equipment:

   - Dry grinding jaw crusher, ball-mills or Raymond® mills.
   - Mixing ground rock with sulfuric acid and water in cone mixers and pug-mills.
   - "Denning," or reaction of the acid-rock paste in specially constructed "dens" or reaction chambers.
   - Slicing the "denned" product into transportable lumps.
   - Curing the lump product in storage piles.
   - Grinding the cured product in tube mills.

2. Input Materials - Based on one metric ton of normal superphosphate produced:

   - Pulverized phosphate rock (~34% P_2O_5): 600 to 610 kg.
   - Sulfuric Acid (100% H_2SO_4 basis): 350 to 360 kg
   - Water: ~0.2 m^3.

3. Operating Parmaters

   - Process is conducted at atmospheric pressure.
   - Highest temperatures attained in process are estimated to be 80 to 100°C in cone mixer and pug-mill, and 100 to 120°C in den.
   - Quantity of water used is varied to produce a substantially dry end-product.
   - Particle size of pulverized rock is usually 50 to 95% minus 200-mesh.
   - Residence time of acid-rock paste in pug-mill is ~2 minutes and ~1 hour in den.
   - Necessary curing time in storage pile is 8 to 10 weeks.
   - Usually no attempt is made to beneficially recover the HF and SiF_4 evolved as gases from the den. Off-gases from den are absorbed in water in a scrubber tower, and scrubber effluent discharged into bed

4. Utilities - Based on one metric ton of normal superphosphate produced:

- Electrical energy: 0.2 to 0.4 kWh.
- Scrubber water: estimated here at 0.5 to 1.5 m^3.

5. Waste Streams - Particulate atmospheric emissions of ~200-mesh phosphate rock from grinding equipment is surmised. No quantifying information is available. Quantity estimated at <1 kg per metric ton of normal superphosphate produced.

Effluent scrubber water, containing both HF and H_2SiF_6 is run into beds of limestone to precipitate CaF_2. The latter is considered here to be solid waste. Quantities involved, per metric ton of normal superphosphate, are estimated to be:

- Scrubber water: 0.5 to 1.5 m^3.
- Total fluorine recovered in limestone bed: 8 to 10 kg.

Information was not available on the efficiency of scrubbers in removing gaseous contaminants.

6. EPA Source Classification Code

3-01-028-01	Grind-dry
3-01-028-02	Main stack

7. References

Faith, W. L., D. B. Keyes, and R. L. Clark. Industrial Chemicals, 3rd Edition. New York, John Wiley & Sons, 1965. p. 194-195.

Shreve, R. N. Chemical Process Industries, 3rd Edition. New York, McGraw-Hill, 1967. p. 270-271.

Slack, A. V. Fertilizers. In: Kirk-Othmer Encyclopedia of Chemical Technology, 2nd Edition. Standen, A. (ed.). New York, Interscience Publishers, 1966. 9:100-106.

Wang, K-L., B. W. Klein, and A. F. Powell. Economic Significance of the Florida Phosphate Industry, Information Circular 8653. Washington, U. S. Bur. Mines., 1974. p. 46.

Wet-Acid Process

1. Function - The process (See Figure 2) produces ortho-phosphoric acid (H_3PO_4) by digesting phosphate rock or phosphate rock concentrates from Process 2 or 3, with sulfuric acid from Process 7: $CaF_2 \cdot 3Ca_3(PO_4)_2 + 10H_2SO_4 + 20\,H_2O \rightarrow 6H_3PO_4 + 10CaSO_4 \cdot 2H_2O + 2HF$.

   The phosphoric acid produced may be transferred to either Process 6, Figure 2; Process 27 or 28, Figure 6; or to Process 40 or 44, Figure 9,

   At least two variations of the basic process embodying the above reaction are commercial: The hemihydrate process and the dihydrate process. The latter is the one considered here.

   The process includes the following essential steps and major equipment:

   - Dry-grinding the input phosphate rock in hammer mills.
   - Reaction (digestion or dissolution) of the ground phosphate rock with sulfuric acid in carbon-lined, closed reaction tanks.
   - Filtration of the resulting slurry on a specially designed, continuous, tilting-pan filter to remove gypsum crystals.
   - Concentration of clear phosphoric acid to marketable strength in vacuum evaporators.
   - Recovery (optional) of the fluorine values of the input rock as H_2SiF_6 in off-gas scrubbing equipment.

   The process embodies many recycle flows and equipment not mentioned in the above over-simplified summary.

   If beneficially recovered, both the gypsum and the fluorosilicic acid formed in the process are industry by-products.

2. Input Materials - Based on one metric ton of 75% ortho phosphoric acid produced:

   - Phosphate rock (~32% P_2O_5): 1.76 metric tons
   - Sulfuric acid (~93% H_2SO_4): 1.53 metric tons

3. Operating Parameters

   - Most steps are conducted at atmospheric pressure. Vacuum evaporators operate at ~0.1 to 0.2 kg/cm^2 absolute pressure.
   - Highest temperature attained is ~135°C (in H_2SO_4 dilution tank). Temperatures in most other equipment are between 40 and 80°C.
   - Phosphate rock is ground to 100% minus 40-mesh.

- Approximately 25% of total fluorine values entering with rock leaves process with gypsum, 12% in product acid. The remainder may be recovered.
- If fluorine values are not beneficially recovered, off-gases from digestion are absorbed in $Ca(OH)_2$ scrubber. CaO is added as make-up, estimated to be 180 kg per metric ton of 75% phosphoric acid produced.

4. Utilities - Based on one metric ton of 75% ortho phosphoric acid produced:

- Steam at 3 kg/cm^2 pressure: 0.8 metric tons
- Steam at 10 kg/cm^2 pressure: 25 kg
- Cooling water: ~75 m^3 (once-through basis)
- Process water: 3.8 to 4.0 m^3
- Electrical energy: ~50 kWh

5. Waste Streams - Referred to one metric ton of 75% ortho phosphoric acid produced:

- Particulates of phosphate rock discharged to atmosphere from hammermills (surmised): Estimated at <5 kg.
- Gypsum: 2.5 metric tons (contains ~0.5% F). This is discharged, along with 1.1 m^3 of spent process water, into ponds or onto waste piles. A small fraction may be sold for soil conditioning.
- Fluorine: ~40 kg.
  Fluorine values are discharged in form of CaF_2, along with ~160 kg of $Ca(OH)_2$, slurried in 35 m^3 of water.
- Size of a single installation may vary from 200 to 1500 metric tons per day of 75% phosphoric acid.

6. EPA Source Classification Code

3-01-016-01	Reactor-uncontrolled
3-01-016-02	Gypsum pond
3-01-016-03	Condenser-uncontrolled

7. References

Faith, W. L., D. B. Keyes, and R. L. Clark. Industrial Chemicals, 3rd Edition. New York, John Wiley & Sons, 1965. p. 603-605.

Haddeland, G. E. Wet Phosphoric Acid Process. Process Economics Program Report 8B. Menlo Park, Stanford Research Institute, 1974. p. 43-75.

Shreve, R. N. Chemical Process Industries, 3rd Edition. New York, McGraw-Hill, 1967. p. 273-274.

Slack, A. V. Fertilizers. In: Kirk-Othmer Encyclopedia of Chemical Technology, 2nd Edition. Standen, A. (ed.). New York, Interscience Publishers, 1966. 9:86-100.

Wang, K-L., B. W. Klein, and A. F. Powell. Economic Significance of the Florida Phosphate Industry, Information Circular 8653. Washington, U. S. Bur. Mines, 1974. 51 p.

TSP Process

1. Function - The process (See Figure 2) produces triple superphosphate (TSP) by reacting either phosphate rock concentrates or high-grade phosphate rock from Process 2 or 3, with phosphoric acid from Process 5: $CaF_2 \cdot 3Ca_3(PO_4)_2 + 14H_3PO_4 \rightarrow 10CaH_4(PO_4)_2 + 2HF$.

   The conversion represented by the above reaction is conducted commercially by either of two processes. One uses a process almost identical with that for the production of normal superphosphate (See Process 4). The other employs a combined acidification-granulation technique. The latter process is described here.

   The process employs the following steps and equipment:

   - Pulverizing the phosphate rock in ball-mills.
   - Pre-heating the phosphoric acid.
   - Reacting the rock with acid in a revolving cylindrical reactor; the acid is injected into the burden of recycled fines and input fine rock. Steam is also injected. Granulation occurs in the reaction cylinder.
   - Cooling the reactor product in a rotary cooler.
   - "Curing" the cooled product in storage pile.

   Usually no attempt is made to beneficially recover the fluorine values evolved as gases from the reactor.

   The product is either marketed for direct use as a fertilizer or is transferred to Process 30 or 32, Figure 7.

2. Input Materials - Based on one metric ton of triple superphosphate:

   - Pulverized phosphate rock (~34% P_2O_5): 420 to 440 kg.
   - Phosphoric Acid (53% P_2O_5): 490 to 510 kg.

3. Operating Parameters

   - Process is conducted at atmospheric pressure.
   - Estimated maximum temperatures are 60°C in acid preheater and 100°C in granulator/reactor drum.
   - Particle size of input rock is 70% minus 200-mesh.
   - Necessary curing time in storage pile is 10 to 20 days.
   - Typical installation produces 500 to 900 metric tons of product per day.
   - Limestone bed is used to treat scrubber effluent.

4. Utilities - Referred to one metric ton of triple superphosphate:

- Water to reactor off-gas scrubber: Estimated at 0.5 to 1.5 m^3.
- Steam to granulator reactor: 40 to 50 kg.
- Electrical energy: 40 to 45 kWh.

5. Waste Streams

- Particulates of phosphate rock to atmosphere from grinding equipment are surmised. Quantity estimated to be <5 kg per metric ton of triple superphosphate.

- 0.5 to 1.5 m^3 of scrubber water per metric ton of triple superphosphate. This flow is discharged into limestone bed, where an estimated 10 to 12 kg of fluorine per metric ton of triple superphosphate is precipitated as CaF_2.

6. EPA Source Classification Code

3-01-029-02 Granular

7. References

Faith, W. L., D. B. Keyes, and R. L. Clark. Industrial Chemicals, 3rd Edition. New York, John Wiley & Sons, 1965. p. 195-196.

Shreve, R. N. Chemical Process Industries, 3rd Edition. New York, McGraw-Hill, 1967. p. 272-273.

Slack, A. V. Fertilizers. In: Kirk-Othmer Encyclopedia of Chemical Technology, 2nd Edition. Standen, A. (ed.). New York, Interscience Publishers, 1966. 9:106-109.

Wang, K-L., B. W. Klein, and A. F. Powell. Economic Significance of the Florida Phosphate Industry, Information Circular 8653. Washington, U. S. Bur. Mines, 1974. p. 47.

Sulfuric Acid Manufacture

1. Function - This process (See Figure 2) produces sulfuric acid (H_2SO_4) from sulfur, air, and water by oxidation of the sulfur in air followed by absorption of sulfur trioxide (SO_3) into wet sulfuric acid (H_2SO_4). The H_2SO_4 produced goes to:

   - Sales (Figure 2)
   - Normal superphosphate processing (Process 4, Figure 2)
   - The wet-acid process (Process 5, Figure 2)
   - Ammonium sulfate formation (Process 21, Figure 4)
   - Ammonium phosphate or nitric phosphate processing (Processes 27 and 28, Figure 6)
   - Ammoniation/granulation/drying (Process 30, Figure 7)

   Molten sulfur from the Frasch mining process (or from hydrocarbons using the Claus process) is filtered and then burned in dry, compressed air. The resulting combustion gases containing 12 percent sulfur dioxide (SO_2) are cooled, mixed with more air, and fed to a four-stage catalyst converter. As the gas passes through the first catalyst bed, some of the SO_2 is converted to SO_3 in an exothermic reaction. The gas is then cooled and passed through the second catalyst bed where more SO_2 is converted to SO_3. The gas is then cooled and may be passed through an absorber countercurrent to 98+ percent H_2SO_4. Most of the SO_3 is absorbed into the H_2SO_4. The unabsorbed gas goes to the third catalyst bed where most of the remaining SO_2 is converted to SO_3. The gas is then cooled, goes to the fourth catalyst bed, is recooled, and then passes through another absorber where SO_3 is absorbed into 98+ percent H_2SO_4.

   Sulfuric acid manufacture has been described in more detail in another chapter.

2. Input Materials

   - Sulfur - 0.33 metric tons per metric ton sulfuric acid product
   - Air - 8,000 cubic meters per metric ton H_2SO_4
   - Water - 0.2 cubic meters per metric ton H_2SO_4

3. Operating Parameters (for 900-metric ton per day plant)

   - Molten sulfur storage - 20 meters diameter x 10 meters high.
   - Storage temperature - 140°C.
   - Sulfur filter - Steam jacketed; vertical pressure leaf type.
   - Air drying tower - 10 meters high x 5 meters diameter, lined with acidproof brick.
   - Air blower - 1500 kW.
   - Sulfur burner - 5 meters diameter x 13 meters long, lined with insulating and fire brick.

- Temperature of exiting gases from sulfur burner - 1120°C.
- Converter - 11 meters diameter x 10 meters tall.
- Converter catalyst - oxides of vanadium, potassium, and silicon.
- Conversion of SO_2 to SO_3 in converter.
  - First stage - 68 percent
  - Second stage - 88 percent
  - Third stage - 98+ percent
  - Fourth stage - 99.5 percent
- Converter temperature.
  - First stage - 425°C to 600°C
  - Second stage - 460°C to 515°C
  - Third stage - 440°C to 470°C
  - Fourth stage - 440°C to 445°C
- Interstage absorber - 10 meters tall x 5 meters diameter, lined with acidproof brick.
- Final absorber - 10 meters tall x 4.5 meters diameter, lined with acidproof brick.

4. Utilities

- Cooling water - 35 to 45 cubic meters per metric ton sulfuric acid.
- Electrical energy - 10 kWh per metric ton sulfuric acid.
- Filter acid - 0.1 kg per metric ton sulfuric acid.
- Steam production - 0.5 to 0.8 metric tons of 28 kg/cm^2 steam produced per metric ton sulfuric acid and 0.4 to 0.6 metric tons of 5 to 6 kg/cm^2 steam produced per metric ton sulfuric acid.

5. Waste Streams - Tail gas from H_2SO_4 plants is approximately 2 metric tons per metric ton H_2SO_4 produced. SO_2 in the tail gas amounts to approximately 4 kg per metric ton H_2SO_4 for conventional single absorber plants. SO_2 in the tail gas of old plants may be 14 kg per metric ton H_2SO_4. SO_2 in the tail gas of plants employing double absorption amounts to approximately 0.5 kg per metric ton H_2SO_4. Particulates in the tail gas may amount to 1.3 kg per metric ton H_2SO_4.

6. EPA Classification Code

3-01-023-08 98.0 Conversion

7. References

Faith, W. L., D. B. Keyes, and R. L. Clark. Industrial Chemicals, 3rd Edition. New York, John Wiley & Sons, Inc., 1965. p. 746-756.

Ries, H. C. Sulfuric Acid. Stanford Research Institute, Menlo Park, California. Process Economics Program, Report No. 84. February 1973. 270 p.

Phosphate Rock Calcination

1. Function - This process (See Figure 2) blends phosphate rock concentrate from Process 2 or 3 with phosphoric acid, silica, and caustic soda or sodium chloride, pugs the blend to a thick slurry, dries the slurry, agglomerates the dried slurry to a 1 cm x 20 mesh material, and defluorinates the material in rotary kilns or fluid-bed reactors. The defluorinated product is used as an animal or poultry feed supplement after being ground.

2. Input Materials

   - Either beneficiated phosphate rock concentrate or unbeneficiated high-grade phosphate rock - 0.6 to 0.8 metric tons.
   - Phosphoric acid - 0 to 0.1 metric tons.
   - Silica - 0.2 to 0.4 metric tons.
   - Sodium hydroxide - no information available.
   - Sodium chloride - no information available.

3. Operating Parameters

   - Initial fluorine content in phosphate rock concentrate ~3.5 percent.
   - Final fluorine content in defluorinated material <0.2 percent.
   - Kiln or fluid-bed reactor temperature is 1400 to 1540°C.

4. Utilities

   - Electrical energy - 20 kWh per metric ton defluorinated rock.
   - Fuel for drying and defluorinating - 2 x 10^6 kcal per metric ton defluorinated rock.

5. Waste Streams - Effluent gases contain fluorine primarily as hydrogen fluoride and to a lesser extent as silicon tetrafluoride. The fluorine may be recovered to produce fluorine chemicals. The amount of fluorine in the gases is approximately 0.03 metric tons per metric ton defluorinated rock. No quantitative information on the amount released to the atmosphere is available.

6. EPA Classification Code - None exists.

7. References

Payne, J. H. Chapter 17. In: Phosphorus and Its Compounds. Van Wazer, J. R. (ed.). New York, Interscience Publishers, Inc. 1961. 2:1090-1092.

Wang, K. L., B. W. Klein, and A. F. Powell. Economic Significance of the Florida Phosphate Industry. Information Circular 8653, Bureau of Mines, Washington, U. S. Government Printing Office, 1974. p. 47.

AMMONIA SYNTHESIS

The processes in this operation are those which are used for the synthesis of ammonia. Ammonia is produced from ammonia synthesis gas consisting of 75% hydrogen and 25% nitrogen on a mole basis. Nitrogen is obtained from air by liquefaction and distillation or by combustion of hydrogen to remove oxygen. Hydrogen may be obtained by several alternate methods. These methods include purification of hydrogen rich streams derived from other processes (coke oven gas, refinery off-gas or electrolytic hydrogen) and synthesis from hydrocarbons. The most common methods of producing hydrogen for ammonia synthesis are by partial oxidation of hydrocarbons followed by shift conversion or by steam reforming of hydrocarbons.

Several methods of obtaining ammonia synthesis gas are described in the following process descriptions. In general a given ammonia production facility will have available only one or two of the possible hydrogen producing feedstocks and will obtain hydrogen by the most economic method available. The bulk of hydrogen production comes from methane or other light hydrocarbons.

Carbon Dioxide is produced and may be vented or used for urea production.

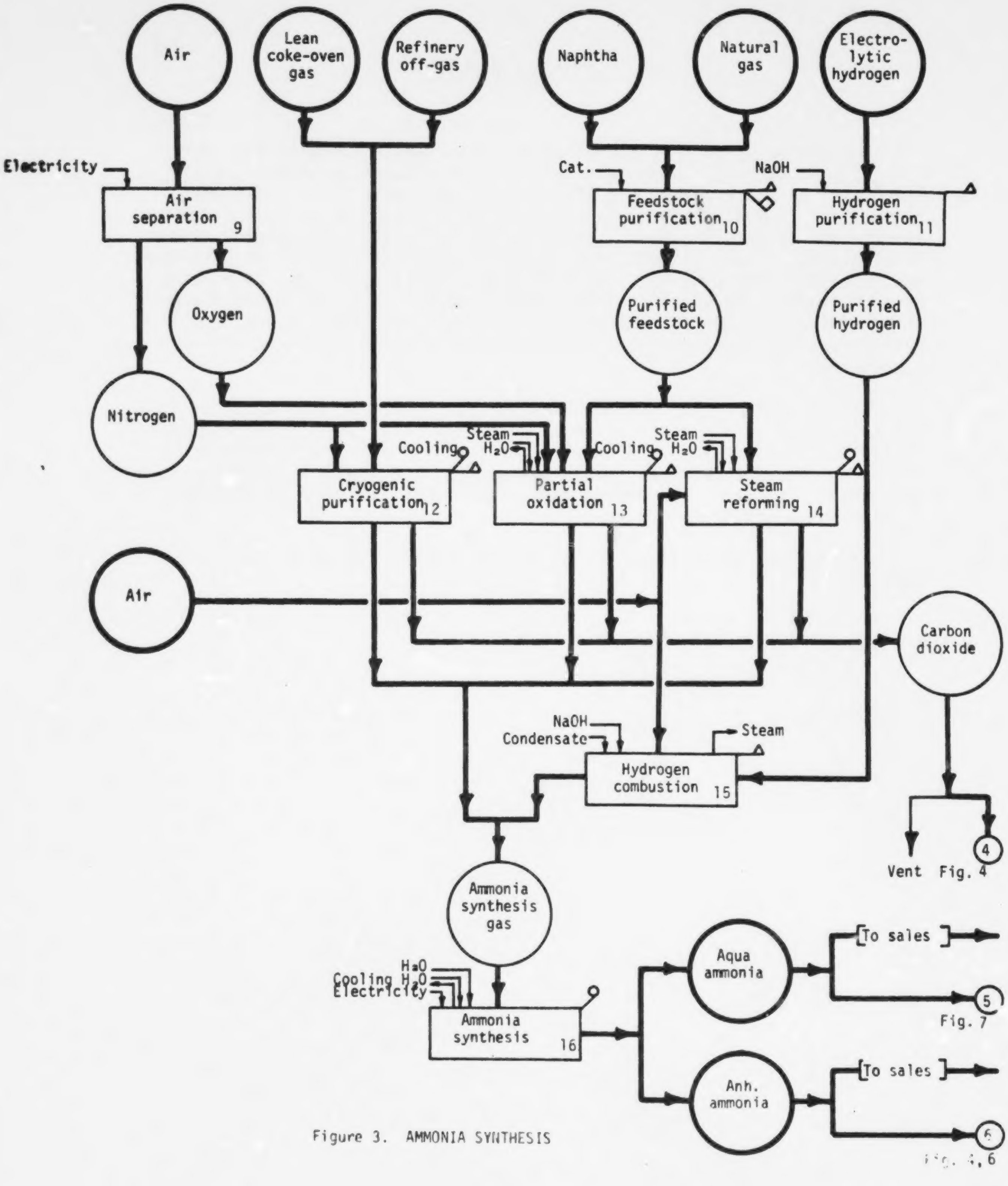

Air
Lean coke-oven gas
Refinery off-gas
Naphtha
Natural gas
Electro-lytic hydrogen
Electricity
Air separation 9
Cat.
Feedstock purification 10
NaOH
Hydrogen purification 11
Oxygen
Purified feedstock
Purified hydrogen
Nitrogen
Steam
Cooling
H₂O
Cryogenic purification 12
Partial oxidation 13
Steam
Cooling
H₂O
Steam reforming 14
Air
Carbon dioxide
NaOH
Condensate
Steam
Hydrogen combustion 15
Vent
4
Fig. 4
Ammonia synthesis gas
H₂O
Cooling H₂O
Electricity
Ammonia synthesis 16
Aqua ammonia
To sales
5
Fig. 7
Anh. ammonia
To sales
6
Fig. 4,6

Figure 3. AMMONIA SYNTHESIS

Air Separation

1. Function - This process (See Figure 3) separates air into its components. The two primary products are nitrogen (N_2) and oxygen (O_2). The separation is accomplished by compressing, cooling, purifying, and distilling the air. Nitrogen product goes to:

   - Cryogenic purification (Process 12, Figure 3)
   - Partial oxidation (Process 13, Figure 3)

   Oxygen product goes to:

   - Partial oxidation (Process 13, Figure 3)

   Air is compressed and then cooled by a series of heat exchangers with water, freon, and exiting cold nitrogen and oxygen products. Moisture, hydrocarbons, and carbon dioxide are removed at several places between the cooling steps by passing the air through water-oil separators, alumina driers, CO_2 adsorbers, and hydrocarbon filters. Nitrogen and oxygen are then separated from each other in a two-section distillation column. The cooling value in each product stream is recovered by using it to cool entering air feed to the process.

2. Input Materials

   - Air - 2000 cubic meters per metric ton NH_3.

3. Operating Parameters

   - Air pressure after compression - 175 kg/cm^2.
   - Temperature of air entering high pressure section of distillation column - 100°K.
   - Pressure in high pressure section of distillation column - 7 kg/cm^2.
   - Temperature inside low pressure section of distillation column - 80 to 90°K.
   - Pressure in low pressure section of distillation column - 1.6 to 2 kg/cm^2.

4. Utilities

   - Electrical energy - 300 kWh per metric ton NH_3.
   - Cooling water - 15 cubic meters per metric ton NH_3.

5. Waste Streams - None exists.

6. EPA Classification Code - None exists.

7. References

Latimer, R. E. Distillation of Air. Chemical Engineering Progress. 63:35-59, February 1967.

Saxton, J. C., M. P. Kramer, D. L. Robertson, M. A. Fortune, N. E. Leggett, and R. G. Capell. Data Base for the Industrial Energy Study of the Industrial Chemicals Group. Dept. of Commerce, Washington. Publication No. PB-237-845. September 1974. 242 p.

Ammonia Feedstock Purification

1. **Function** - This process (See Figure 3) removes sulfur compounds from natural gas or naptha so that these materials can be used as feedstock in the production of ammonia. The purified feedstock materials are fed to partial oxidation (Process 13) or steam reforming (Process 14).

   Natural gas, the dominant feedstock for ammonia, is desulfurized by passing the gas over activated carbon or zinc oxide adsorbents. Activated carbon can be used at ambient temperature while the gas must be preheated to above 350°C for efficient adsorption by zinc oxide. Activated carbon is regenerated by steam stripping whereas zinc oxide must be replaced when it reaches 15 weight percent sulfur.

   Naphtha requires hydrodesulfurization. Hydrogen and vaporized naphtha are mixed and heated to 320°C. The mixture is then passed over a cobalt-molybdenum catalyst where the sulfur compounds are converted to hydrogen sulfide. The gas is then passed over a sulfur adsorbent such as iron or zinc oxide.

2. Input Materials

   - 600 to 800 cubic meters natural gas per metric ton ammonia or 0.8 cubic meters naphtha per metric ton ammonia.
   - Adsorbent - up to 0.2 kg zinc oxide per metric ton ammonia or 0.05 kg activated carbon per metric ton ammonia.

3. Operating Parameters

   - Sulfur content of natural gas
     - Before desulfurization - usually below 65 ppm.
     - After desulfurization - below 0.2 ppm.
   - Desulfurization drums containing zinc oxide - 2.5 meters diameter x 3.5 meters tall containing 16 m^3 of zinc oxide catalyst for plant producing 1500 metric tons ammonia per day.
   - Temperature
     - 400°C for zinc oxide adsorbent.
     - Ambient for activated carbon adsorbent.
   - Pressure - 30 to 40 kg/cm^2
   - Two-month life for zinc oxide adsorbent.
   - 1 m^3 activated carbon adsorbent treats 100,000 to 200,000 m^3 gas.
   - Steam for carbon regeneration - 0.8 to 1.6 metric tons per m^3 carbon.
   - Greater than 2-year life expectancy of activated carbon.

4. Utilities

   - Fuel for preheating natural gas in case of zinc oxide adsorbent - 100,000 kcal per metric ton ammonia.

- Steam for activated carbon regeneration - 0.005 to 0.01 metric tons per metric ton ammonia.

5. Waste Streams

- Zinc oxide adsorbent containing 15 percent sulfur is discarded. It can amount to 0.0002 metric tons per metric ton ammonia produced.

- Condensate from activated carbon regeneration may be discarded. It amounts to 0.005 to 0.01 cubic meters per metric ton ammonia and contains sulfur compounds.

6. EPA Classification Code - None exists.

7. References

Faith, W. L., D. B. Keyes, and R. L. Clark. Industrial Chemicals, 3rd Edition. New York, John Wiley & Sons, Inc. 1965. p. 443.

Green R. V. Chapter 5. In: Riegel's Handbook of Industrial Chemistry, 7th Edition. Kent, J. A. (ed.). New York, Van Nostrand Reinhold Company, 1974. p. 78-84.

Muller, R. G. Ammonia. Report No. 44, Process Economics Program. Stanford Research Institute, Menlo Park, California. November 1968. 235 p.

Hydrogen Purification

1. Function - This process (See Figure 3) receives electrolytic hydrogen as a by-product from sodium chloride brine electrolysis and removes impurities so that the hydrogen can be used to form ammonia synthesis gas in Process 15.

   The hydrogen from brine electrolysis contains minor amounts of carbon dioxide and chlorine. These are washed out by passing the hydrogen countercurrent to a recirculating dilute caustic solution in a packed tower. Hydrogen leaving the column is saturated with water vapor.

2. Input Materials

   - 2500 cubic meters wet hydrogen per metric ton ammonia (2300 cubic meters dry hydrogen).
   - 1 kg sodium hydroxide (10% basis) per metric ton ammonia.

3. Operating Parameters

   - Impurity content of hydrogen from chlorine cells is less than 100 ppm (dry basis).
   - Washing temperature - 30°C.
   - Pressure - 1.5 kg/cm^2

4. Utilities - Negligible

5. Waste Streams - Scrubbing solution is discarded. It amounts to 1 kg per metric ton ammonia and contains sodium hydroxide, sodium carbonate, sodium hypochlorite, and sodium chloride.

6. EPA Classification Code - None exists.

7. References

Green, R. V. Chapter 5. In: Riegel's Handbook of Industrial Chemistry, 7th Edition. Kent, J. A. (ed.). New York, Van Nostrand Reinhold Company, 1974. p. 87.

Pauling, L. General Chemistry, 2nd Edition. San Francisco, W. H. Freeman and Company, 1953. p. 268-269.

Yen, Y. C. Chlorine, Supplement A. Report No. 61A, Process Economics Program. Stanford Research Institute, Menlo Park, California. May 1974. p. 74-75.

Cryogenic Purification

1. Function - This process (See Figure 3) removes impurities from hydrogen rich gases (refinery off-gas or coke-oven gas) and mixes nitrogen with the purified hydrogen. The resulting ammonia synthesis gas goes to ammonia synthesis, Process 16.

   Refinery off-gases usually contain 75 to 95 mol percent hydrogen. Hydrogen sulfide and carbon dioxide are removed by caustic scrubbing. Then the gas is dried over activated alumina to a dew point of -70°C. It is then cooled, separated from liquefied hydrocarbons, and scrubbed with liquid nitrogen (which has been obtained by compressing, cooling, and expanding nitrogen from air separation, Process 9) to remove any remaining hydrocarbons plus carbon monoxide. The overhead from the scrubbing column consists of 90 mol percent hydrogen and 10 mol percent nitrogen. Additional gaseous nitrogen is added to give a 75 to 25 mol ratio. As much as possible, the cooling value present in all streams is used to cool incoming streams. Separated hydrocarbons including the bottoms from the scrubber are used as fuel.

   Coke-oven gases usually contain 55 to 60 mol percent hydrogen after by-product coke-oven chemicals (ammonia, light oils, naphthalene) are removed. Further purification processes are similar to those described for the refinery off-gases.

2. Input Materials

   - 2050 to 2800 cubic meters cracker off-gas per metric ton ammonia or 3500 cubic meters coke-oven gas per metric ton ammonia.
   - 700 cubic meters nitrogen per metric ton ammonia.
   - 10 kg sodium hydroxide (10% basis) per metric ton ammonia.

3. Operating Parameters

   - Nitrogen scrubber pressure - 15 to 30 kg/cm^2.
   - Nitrogen scrubber temperature - 185°C.
   - Synthesis gas purity - 10 ppm oxygenated compounds and 150 to 200 ppm of inerts in the form of argon plus methane.
   - Nitrogen liquefaction conditions:
     - Compressed to 200 kg/cm^2.
     - Cooled with cooling water.
     - Expanded to 30 kg/cm^2.
   - Typical bottoms composition from nitrogen scrubber:
     - 5-10 mol percent hydrogen.
     - 30-60 mol percent nitrogen.
     - 0-15 mol percent carbon monoxide.
     - 10-60 mol percent methane.

- Nitrogen scrubber - 0.6 meters inner diameter x 9 meters tall for plant producing 90 metric tons ammonia per day.

4. Utilities

- Electricity - 200 kWh per metric ton ammonia.
- Cooling water - 35 cubic meters per metric ton ammonia.

5. Waste Streams

- The dilute caustic scrubbing solution is discarded. It contains sodium carbonate, sodium hydroxide, and sodium sulfide and is estimated to be 10 kg per metric ton ammonia.
- The bottoms stream from the nitrogen scrubbing column is vaporized and used as fuel. It amounts to 100 to 200 cubic meters per metric ton ammonia and contains methane. nitrogen, carbon monoxide, and hydrogen.

6. EPA Classification Code - None

7. References

Arnold, J. H., and W. T. Dixon. From By-Product Hydrogen to Anhydrous Ammonia. Petroleum Processing. 11:62-66, January 1956.

Baker, D. F. Low-Temperature Processes. Chem. Eng. Progr. 51:399-402, September 1955.

Bardin, J. S., and D. W. Beery. Producing Ammonia Synthesis Gas. Petroleum Refiner. 32:99-102, February 1953.

Partial Oxidation

1. Function - This process (See Figure 3) receives purified natural gas or naphtha from feedstock purification (Process 10) along with oxygen insufficient for complete combustion and steam. Carbon monoxide and hydrogen form and are sent to a shift converter where an impure hydrogen stream is formed. This stream is purified and mixed with nitrogen to form ammonia synthesis gas which is forwarded to ammonia synthesis, Process 16.

   A preheated mixture of hydrocarbon feed and steam mixes with a preheated oxygen stream (from air separation, Process 9) in a reactor. The oxygen burns with a portion of the feed in an exothermic flame front. Unreacted hydrocarbon then reacts with the water and carbon dioxide in endothermic reactions to produce hydrogen and carbon monoxide. The exiting gas stream is cooled and passed through a catalytic shift converter where water reacts with carbon monoxide to form carbon dioxide and hydrogen. Cooling of the converter exiting stream allows water to condense and then carbon dioxide is removed by absorption into an absorbing solution such as ethanolamine or potassium carbonate. (Regeneration of the absorbing solution produces carbon dioxide rich gas which is vented or sent to Process 19, Figure 4). The fairly pure 96 percent hydrogen stream is then further purified by scrubbing with liquid nitrogen (which has been obtained by compressing, cooling, and expanding nitrogen from air separation, Process 9). The overhead from the nitrogen scrubbing column is approximately 95 mol percent hydrogen and 5 mol percent nitrogen. Gaseous nitrogen is added to this stream to give a 75 mol percent hydrogen composition. The bottoms from the nitrogen scrubber are used as fuel.

2. Input Materials

   - 0.8 cubic meters naphtha per metric ton ammonia or 600 to 800 cubic meters natural gas per metric ton ammonia.
   - 500 cubic meters oxygen per metric ton ammonia.
   - 3 cubic meters water per metric ton ammonia.
   - 750 cubic meters nitrogen per metric ton ammonia.
   - 0.1 kg partial oxidation catalyst per metric ton ammonia.
   - 0.1 kg low temperature shift catalyst per metric ton ammonia.
   - 0.3 kg potassium carbonate absorbent per metric ton ammonia.

3. Operating Parameters

   - Partial oxidation reactor (with catalyst)
     Feed temperature - 550°C; outlet tempeature - 870°C.

Pressure - 20 kg/cm^2.
Equipment - 4 meters diameter x 15 meters tall containing two beds 3 meters deep of nickel oxide catalyst of 30m^3 volume each for 700 metric tons ammonia per day plant.

- Shift converter
  Temperature - 250 to 300°C.
  Pressure - 16 kg/cm^2.
  Equipment - 2 meters diameter x 12 meters tall containing two 3 meter-deep beds of catalyst, of 7m^3 volume each for a 700-metric tons-ammonia per day plant.
- Liquid nitrogen scrubber
  0.6 meters inner diameter x 9 meters tall for plant producing 100 metric tons ammonia per day.

- Partial oxidation reactor (without catalyst)
  Pressure - up to 100 kg/cm^2.
  Temperature - 1400°C.

4. Utilities

- Naphtha fuel - 700,000 kcal per metric ton ammonia.
- Cooling water - 150 cubic meters per metric ton ammonia.
- Steam - 0.3 metric tons per metric ton ammonia.
- Electricity - 200 kWh per metric ton ammonia.

5. Waste Streams

- The bottoms stream from the nitrogen scrubbing column is vaporized and used as fuel. It amounts to 100 cubic meters per metric ton ammonia and contains methane, nitrogen, carbon monoxide, and hydrogen.

- Carbon dioxide rich gas may be vented from the potassium carbonate solution regenerator. This stream amounts to 1.2 metric tons carbon dioxide per metric ton ammonia.

- Waste water amounting to 0.1 cubic meters per metric ton ammonia may be released from the carbonate solution regenerator.

6. EPA Classification Code

3-01-003-01	Regenerator Exit

7. References

Bardin, J. S., and D. W. Beery. Producing Ammonia Synthesis Gas. Petroleum Refiner. 32:99-102, February 1953.

Green, R. V. Chapter 5. In: Riegel's Handbook of Industrial Chemistry, 7th Edition. Kent, J. A. (ed.). New York, Van Nostrand Reinhold Company, 1974. p. 86-89.

Haddeland, G. E. Hydrogen. Report No. 32A, Process Economics Program. Stanford Research Institute, Menlo Park, California. December 1973. 397 p.

Muller, R. G. Ammonia. Report No. 44, Process Economics Program. Stanford Research Institute, Menlo Park, California. November 1968. 237 p.

Steam Reforming

1. Function - This process (See Figure 3) receives purified natural gas or naphtha from feedstock purification (Process 10) along with air and steam. Reforming and shift reactions result in the formation of impure ammonia synthesis gas which is purified and sent to ammonia synthesis, Process 16.

   Desulfurized natural gas is preheated to 540°C and fed with steam (at a 4 to 1 steam to gas weight ratio) to a tubular furnace. The mixed gases pass over a nickel reforming catalyst located inside gas-heated furnace tubes. Approximately 75 percent of the methane is converted to hydrogen and carbon oxides by reforming and shift reactions. The hot gas still contains some methane. It is mixed with preheated air and after combustion occurs, the hot gas proceeds through a bed of nickel reforming catalyst. The hot (975°C) exiting gas is cooled below 370°C and passed over an iron catalyst and then a copper-zinc catalyst at 220°C where carbon monoxide is shifted to carbon dioxide. The shifted gas is passed through an absorbing solution where CO_2 is removed. The CO_2 is stripped from the absorbing solution and is vented or forwarded to Process 19, Figure 4. The small amount of remaining carbon oxides are converted to methane in a methanator by passing the gas over a nickel catalyst. The gas then consists essentially of nitrogen and hydrogen in a 1 to 3 mol ratio.

   Naphtha is processed similarly to natural gas except that a different reformer catalyst may be used.

2. Input Materials

   - 600 to 800 cubic meters natural gas per metric ton ammonia or 0.8 cubic meters naphtha.
   - 850 to 1000 cubic meters air per metric ton ammonia.
   - 0.7 to 1.0 cubic meters water per metric ton ammonia.
   - 0.1 kg reforming catalyst per metric ton ammonia.
   - 0.1 kg shift catalyst per metric ton ammonia.
   - 0.3 kg potassium carbonate per metric ton ammonia.
   - 0.02 kg methanation catalyst per metric ton ammonia.

3. Operating Parameters (Plant capacity - 1500 metric tons ammonia per day)

   - Primary reforming step
     Temperature
       Inlet - 540°C
       Outlet - 815°C
     Pressure - 28 to 35 kg/cm^2.

Equipment - 420 - 1.8 cm outer diameter x 1.5 cm inner diameter x 13 meter tubes filled with 48 m^3 of catalyst.

- Secondary reforming step
  - Temperature
    - Inlet - 815°C
    - Outlet - 975°C
  - Pressure - 28 to 35 kg/cm^2.
  - Equipment
    - Top section - 2 meters diameter x 3 meters tall
    - Bottom section - 3 meters diameter x 7 meters tall
    - 37 m^3 of catalyst
- Shift conversion step
  - Temperature
    - Inlet first stage - 360°C
    - Outlet first stage - 430°C
    - Inlet second stage - 220°C
    - Outlet second stage - 225°C
  - Pressure - 28 to 35 kg/cm^2
  - Equipment
    - First stage - 4 meters diameter x 10 meters tall
    - Second stage - 4 meters diameter x 11 meters tall
- CO_2 absorber
  - Temperature
    - Inlet - 120°C
    - Outlet - 110°C
  - Pressure - 28 to 35 kg/cm^2
  - Equipment
    - Top section - 2.5 meters diameter x 35 meters tall
    - Bottom section - 4 meters diameter x 30 meters tall
    - Absorbing solution - monoethanolamine or sulfinol or activated potassium carbonate.
- Carbonate solution regenerator
  - Temperature - 115°C
  - Pressure - 2 kg/cm^2
  - Equipment
    - Top section - 3.5 meters diameter x 19 meters tall
    - Bottom section - 2 meters diameter x 9 meters tall
- Methanator
  - Temperature - 315°C
  - Pressure - 25 to 35 kg/cm^2
  - Equipment - 2 meters diameter x 7 meters tall containing 12 m^3 of methanation catalyst (NiO on Al_2O_3)

4. Utilities

- Electrical energy - 50 kWh per metric ton ammonia.
- Fuel primarily for reformers and steam generation (steam is used in Process 16 in addition to this process) - 3.3×10^6 kcal per metric ton ammonia.
- Cooling water - 60 cubic meters per metric ton ammonia.

5. Waste Streams

- Stack gases from the primary reformer may contain criteria pollutants (NO_x and CO). No quantitative data are available.

- Carbon dioxide rich gas may be vented from the carbonate solution regenerator. This stream amounts to 1.2 metric tons carbon dioxide per metric ton ammonia, 0.001 metric tons hydrogen per metric ton ammonia, 0.025 metric tons water per metric ton ammonia with traces of argon, methane, nitrogen, and carbon monoxide.

- Waste water amounting to 0.1 cubic meter per metric ton ammonia may be released from the carbonate solution regenerator.

6. EPA Classification Code

3-01-003-01	Regenerator Exit

7. References

Faith, W. L., D. B. Keyes, and R. L. Clark. Industrial Chemicals, 3rd Edition. New York, John Wiley & Sons, Inc., 1965. p. 77.

Green, R. V. Chapter 5. Riegel's Handbook of Industrial Chemistry, 7th Edition. Kent, J. A. (ed.). New York, Van Nostrand Reinhold Company, 1974. p. 84-90.

Muller, R. G. Ammonia. Report No. 44, Process Economics Program. Stanford Research Institute, Menlo Park, California. November 1968. 235 p.

Hydrogen Combustion

1. Function - This process (See Figure 3) receives purified hydrogen from Process 11 and burns a portion of it in air to produce a gaseous mixture of hydrogen, nitrogen, and water. Water and a small amount of carbon dioxide are removed from the gas before it is forwarded to ammonia synthesis, Process 16.

   Sufficient preheated air is combined with preheated hydrogen so that the combustion products contain nitrogen and hydrogen in a 1 to 3 ratio. The heat of combustion is used to generate steam and preheat the feed gases. The combustion products are further cooled by quenching with water. This is followed by separation of condensed water in a knock-out drum and scrubbing of the gases with dilute caustic to remove the small amount of carbon dioxide brought in with the combustion air.

2. Input Materials

   - 2500 cubic meters wet hydrogen per metric ton ammonia (2300 cubic meters dry hydrogen).
   - 850 cubic meters air per metric ton ammonia.
   - 1 kg sodium hydroxide (10% basis) per metric ton ammonia.

3. Operating Parameters

   - Pressure - 1.1 kg/cm^2
   - Temperature - ambient after scrubbing the combustion products with water.

4. Utilities

   - Steam generation - 1 metric ton per metric ton ammonia.

5. Waste Streams - Scrubbing solution is discarded. It amounts to 1 kg per metric ton ammonia. It contains sodium hydroxide and sodium carbonate.

6. EPA Classification Code - None exists.

7. References

   Green, R. V. Chapter 5. In: Riegel's Handbook of Industrial Chemistry, 7th Edition. Kent, J. A. (ed.). New York, Van Nostrand Reinhold Company, 1974. p. 87.

Ammonia Synthesis

1. Function - This process (See Figure 3) receives purified ammonia synthesis gas from Processes 12, 13, 14, or 15, compresses it, reacts nitrogen with hydrogen to form ammonia, and recovers the ammonia. Either anhydrous ammonia or aqua ammonia can be sold or sent to a number of processes in Figures 4, 6, or 7.

   Synthesis gas, a mixture of hydrogen and nitrogen at a 3 to 1 mol ratio, is compressed in a reciprocating or centrifugal compressor to 150 to 360 kg/cm^2 pressure. It is mixed with recycle synthesis gas from the synthesis converter and refrigerated. Ammonia in the recycle gas condenses and scrubs out any synthesis catalyst poisons in the fresh gas. The condensed ammonia is separated and the gas is further compressed and heated before passing over an iron oxide synthesis catalyst. The gas exiting the synthesis converter is cooled to recover ammonia condensate. Part of the gas is purged to prevent buildup of inerts while the majority is combined with fresh compressed synthesis gas and recycled through the process. The purged gas is used as fuel. The liquid ammonia is sent to a cryogenic storage tank and then loaded on barges, ships, or tank cars for transport to terminals.

2. Input Materials - 2750 cubic meters ammonia synthesis gas per metric ton ammonia.

3. Operating Parameters (1500 metric tons ammonia per day plant)

   - Synthesis pressure - usually 150 to 360 kg/cm^2.
   - Synthesis temperature - usually 400 to 525°C.
   - Synthesis compressor - 26,000 kW, 4 stage compressor.
   - Refrigeration, compressor - 7800 kW, 2 stage compressor.
   - Synthesis converter - 2 meters diameter x 22 meters tall; 2 catalyst beds with internal heat exchanger.
   - Ammonia storage temperature - minus 33°C.
   - Ammonia storage pressure - atmospheric.

4. Utilities

   - Electrical energy - 20 kWh per metric ton ammonia for large plant using steam reformed synthesis gas.
   - Fuel for steam generation - total for steam reforming and ammonia synthesis - 3.3×10^6 kcal per metric ton ammonia.
   - Cooling water - 90 cubic meters per metric ton ammonia.

5. Waste Streams - Purge gas from the reacted synthesis gas stream is 0.1 metric tons per metric ton ammonia gas products. It consists

of methane, nitrogen, hydrogen, argon, and ammonia. It is used as fuel. The ammonia lost is approximately 0.0025 metric tons per metric ton ammonia produced.

6. EPA Classification Code

3-01-002-01	Purge gas
3-01-002-02	Storage/loading

7. References

Green, R. V. Chapter 5. In: Riegel's Handbook of Industrial Chemistry, 7th Edition. Kent, J. A. (ed.). New York, Van Nostrand Reinhold Company, 1974. p. 90-94.

Muller, R. G. Ammonia. Report No. 44, Process Economics Program. Stanford Research Institute, Menlo Park, California. November 1968. 235 p.

PRODUCTION OF AMMONIUM SULFATE, AMMONIUM NITRATE AND UREA

The processes in this operation are those in which sulfuric acid, nitric acid or carbon dioxide are combined with ammonia to produce compounds which are used as fertilizer components.

The process for production of nitric acid from ammonia is included in this operation. Nitrogen oxide emissions from this process constitute one of the environmental problems of the industry.

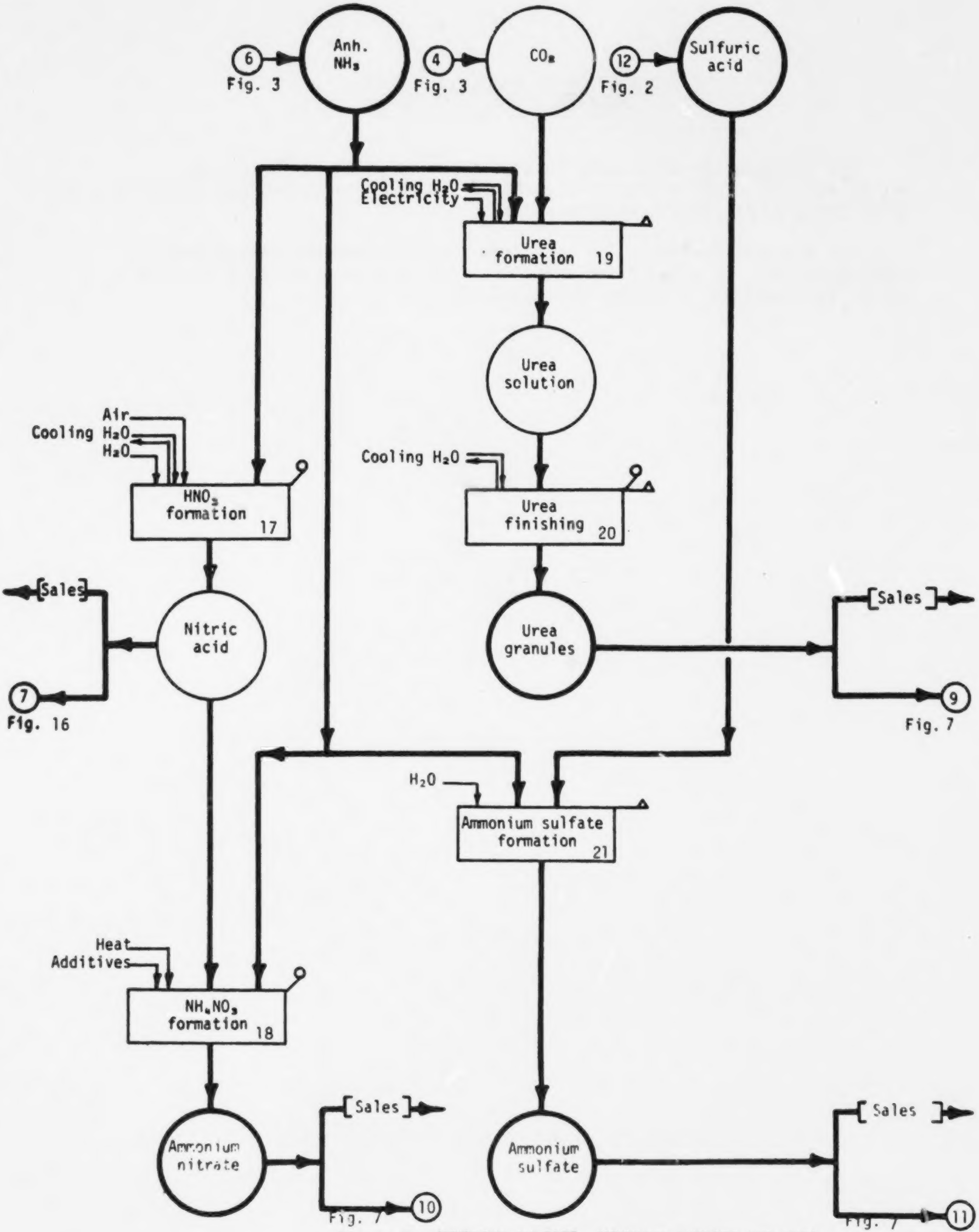

6
Fig. 3
Anh. NH₃
4
Fig. 3
CO₂
12
Fig. 2
Sulfuric acid
Cooling H₂O
Electricity
Urea formation 19
Urea solution
Cooling H₂O
Urea finishing 20
Urea granules
Sales
9
Fig. 7
Air
Cooling H₂O
H₂O
HNO₃ formation 17
Nitric acid
Sales
7
Fig. 16
H₂O
Ammonium sulfate formation 21
Heat
Additives
NH₄NO₃ formation 18
Ammonium nitrate
Sales
Fig. 7
10
Ammonium sulfate
Sales
Fig. 7
11

Figure 4. AMMONIUM SULFATE, AMMONIUM NITRATE AND UREA

HNO_3 Formation

1. Function - This process (see Figure 4) oxidizes ammonia from Process 16, (Figure 3) with air to form nitric oxide. The nitric oxide is further oxidized with air to nitrogen dioxide which is absorbed into water. The resulting nitric acid solution goes either to sales or as input material in the production of ammonium nitrate (Process 18), potassium nitrate (Process 22, Figure 5), ammonium phosphates (Process 27, Figure 6) or nitric phosphate (Process 28, Figure 6).

   The nitric acid process can be conducted at atmospheric pressure or at pressures up to 9 kg/cm^2. The process is similar in either case. Liquid ammonia is vaporized, mixed with preheated air, and introduced into a reactor containing a catalyst bed. Nitric oxide and water are formed in an exothermic reaction and the nitric oxide-air-water vapor mixture (about 10% nitric oxide) is conducted through heat exchangers where air feed to the process is preheated, steam is generated, and feed ammonia is vaporized. The cooled gaseous mixture is then fed along with air to an absorption tower. Water and 40 to 50% nitric acid streams flow countercurrent to the air and nitric oxide stream and absorb nitrogen dioxide which is being formed in an exothermic reaction between air and nitric oxide. External water cooling of the absorption tower is used since low temperature favors nitrogen dioxide formation. The bottoms from the tower is 45 to 65 percent nitric acid. The overhead tail gas is mainly nitrogen. In the case of plants operated above atmospheric pressure, the tail gas can be heated by the hot gaseous reactor products and then run through a turbine to generate power.

   All concentrations of nitric acid may be shipped in stainless steel drums or stainless steel tank trucks or cars.

2. Input Materials

   a. Atmospheric pressure plant

      - 0.15 metric tons ammonia per metric ton 50% nitric acid.
      - 40 mg platinum catalyst per metric ton 50% nitric acid.
      - 0.5 cubic meters process water per metric ton 50% nitric acid.
      - 1750 cubic meters air per metric ton 50% nitric acid.

   b. Pressure plant (8 kg/cm^2)

      - 0.175 metric tons ammonia per metric ton 60% nitric acid.
      - 100 to 200 mg platinum catalyst per metric ton 60% nitric acid.
      - 0.4 cubic meters process water per metric ton 60% nitric acid.
      - 2100 cubic meters air per metric ton 60% nitric acid.

3. Operating Parameters

a. Atmospheric pressure plant

- Temperature in reactor - 800°C.
- Feed to converter - 9.5 to 11% ammonia.
- Product strength - 45 to 52% nitric acid.
- Catalyst - 10% rhodium, 90% platinum alloy gauze made of 0.008 cm diameter wire with 30 meshes to the cm.
- Bubble cap absorption tower operates at 10 to 40°C temperature.

b. Pressure plant

- Temperature in reactor - 900°C.
- Pressure in plant - 8 kg/cm^2
- Feed to converter - 10% ammonia.
- Product strength - 57 to 65% nitric acid.
- Catalyst is same as for atmospheric pressure plant.
- Absorption tower temperature is same as for atmospheric pressure plant.

4. Utilities

a. Atmospheric pressure plant

- Electrical energy - 50 kWh per metric ton 50% nitric acid.
- Steam generation - 0.5 metric ton per metric ton 50% nitric acid.
- Cooling water - 55 cubic meters per metric ton 50% nitric acid.

b. Pressure plant

- Electrical energy - 10 to 250 kWh per metric ton 60% nitric acid.
- Steam generation - 0.5 to .75 metric tons per metric ton 60% nitric acid.
- Cooling water - 75 to 125 cubic meters per metric ton 60% nitric acid.

5. Waste Streams - Tail gas leaving the absorption tower from a pressure plant is passed through an entrainment separator before being heated by hot reactor products. This heated gas may then be passed through a catalytic reduction unit before being expanded in a turbine. If this is done, nitrogen oxide emissions will be approximately 1.7 kg per metric ton of 60% nitric acid. If there is no catalytic reduction unit, nitrogen oxide emissions will be approximately 16 kg per metric ton of 60% nitric acid.

6. EPA Classification Code

3-01-013-01	Ammonia Oxidation Old
3-01-013-02	Ammonia Oxidation New

3-01-013-05	Uncontrolled
3-01-013-06	w/Catyl/Combuster

7. References

Faith, W. L., D. B. Keyes, and R. L. Clark. Industrial Chemicals, 3rd Edition. New York, John Wiley & Sons, Inc., 1965. p. 534-540.

Green, R. V. Chapter 5. In: Riegel's Handbook of Industrial Chemistry, 7th Edition. New York, Van Nostrand Reinhold Company, 1974. p. 94-100.

Heller, A. N., S. T. Cuffe, and D. R. Goodwin. Chapter 38. In: Air Pollution, 2nd Edition. Stern, A. C. (ed.). New York, Academic Press, 1968. 3:203-208.

Shreve, R. N. Chemical Process Industries, 3rd Edition. New York, McGraw-Hill Book Company, 1967. p. 316-321.

NH_4NO_3 Formation

1. Function - This process (See Figure 4) produces ammonium nitrate prills, crystals, and granules by reacting anhydrous ammonia with 60 percent nitric acid and removing water from the reaction product. Ammonium nitrate is sold or used in mixed fertilizers (Figure 7).

   In a typical prilling process, ammonia vapor and nitric acid react in a neutralizing vessel under agitation. The heat of reaction causes water to boil out of the solution and the solution is further concentrated by vacuum evaporation. The resulting 95 percent ammonium nitrate solution is sprayed in the top of a prilling tower. Air rising through the tower solidifies the falling ammonium nitrate into prills. The prills are screened, dried further, dusted with clay to minimize caking tendencies, and screened before storing in a dehumidified building. The product is sold in multi-wall bags or in bulk. The bags must contain at least one layer of plastic or asphalt-impregnated paper to keep moisture from the ammonium nitrate.

   A variation of the typical prilling process is the Stengel process where the ammonia and nitric acid reactants are preheated before feeding to a packed, tubular reactor. A mixture of ammonium nitrate and water leaves the reactor and passes through a cyclone separator. Molten ammonium nitrate flows out the bottom of the separator and can be solidified in a prilling tower. The resulting prills do not require drying. Alternately, the molten ammonium nitrate from the cyclone separator can be solidified on a cooled conveyor belt and the resulting sheet ground or flaked into desired sizes.

   A third process is the continuous vacuum crystallization process. Ammonia gas is introduced below the surface of 60 percent nitric acid and the reaction products charged to vacuum evaporators. The resulting solution goes to vacuum crystallizers. The slurry product from crystallizers is centrifuged and dried in a rotary dryer.

   Sometimes calcium carbonate, ammonium sulfate, or ammonium phosphate is mixed with ammonium nitrate to reduce the explosion hazard of the ammonium nitrate.

2. Input Materials

   - 0.22 metric tons ammonia per metric ton ammonium nitrate.
   - 1.35 metric tons nitric acid (60% concentration) per metric ton ammonium nitrate.
   - 0.02 to 0.03 metric tons clay per metric ton ammonium nitrate.

3. Operating Parameters

- Product moisture - below 0.5%.
- Plant sizes - 25,000 to 400,000 metric tons capacity per year.
- Typical prilling process.
  - Neutralization vessel
    - Temperature - ~130°C
    - Exiting solution concentration - 85%
  - Vacuum evaporator
    - Temperature - 125 to 140°C
    - Exiting solution concentration - 95%
  - Prilling tower
    - Height - 60 meters
    - Exiting prill concentration - 95%
  - Dryers
    - Final moisture content - 0.2%
- The Stengel process
  - Ammonia preheat temperature - 145°C
  - Nitric acid perheat temperature - 165°C
  - Temperature of exiting reactor products - 205°C
  - Moisture content of reactor products - 0.2%
- The continuous vacuum crystallization process
  - Solution concentration leaving neutralizer - 60%
  - Solution concentration leaving vacuum evaporators - 75 to 80%
  - Vacuum crystallizers
    - Temperature - 35°C
    - Pressure - 0.035 kg/cm^2
  - Water content in crystals from centrifuging - 1 to 2%
  - Water content in crystals after drying - 0.05%
  - Highest temperature of crystals in dryer - 60 to 65°C
- Product particle size - 95%: -6 mesh +16 mesh.

4. Utilities

- Electricity - 50 kWh per metric ton ammonium nitrate.
- Steam - 3 metric tons per metric ton ammonium nitrate.
- Cooling water - 15 to 70 cubic meters per metric ton ammonium nitrate.

5. Waste Streams - Emissions occur in neutralization and drying. By keeping the neutralization process on the acidic side, losses of ammonia and nitrogen oxides are kept at a miniumum. Water scrubbers are used in most cases to recover ammonia and ammonium nitrate dust entrained in vent gases from the neutralization tanks, the prilling tower, the dryers, and from other sources. The scrub water is returned to process. Total fines lost can be kept to less than 0.01 metric tons per metric ton ammonium nitrate.

6. EPA Classification Code - None exists.

7. References

Faith, W. L., D. B. Keyes, and R. L. Clark. Industrial Chemicals, 3rd Edition. New York, John Wiley & Sons, Inc., 1965. p. 89-94.

Green, R. V. Chapter 5. In: Riegel's Handbook of Industrial Chemistry, 7th Edition. Kent, J. A. (ed.). New York, Van Nostrand Reinhold Company, 1974. p. 100-101.

Heller, A. N., S. T. Cuffe, and D. R. Goodwin. Chapter 38. In: Air Pollution, 2nd Edition. Stern, A. C. (ed.). New York, Academic Press, 1968. 3:231-234.

Slack. A. V Fertilizers. In: Kirk-Othmer Encyclopedia of Chemical Technology, 2nd Edition. Standen, A. (ed.). New York, John Wiley & Sons, Inc., 1966. 9:59-65.

Urea Formation

1. Function - This process (See Figure 4) combines ammonia and carbon dioxide under high pressure and elevated temperature to form ammonium carbamate. The carbamate is simultaneously dehydrated to form urea and water. The effluent from the urea reactor is an aqueous solution containing urea and unconverted ammonium carbamate. Heating decomposes the carbamate and a resulting gaseous mixture of ammonia, carbon dioxide, and water vapor is separated from a urea-water solution. The urea-water solution goes to urea finishing, Process 20. The gaseous mixture is usually condensed or absorbed into water and recycled to the reactor. In older plants, the gaseous mixture may be utilized to produce ammonium nitrate or sulfate fertilizers.

   Equipment often employed in urea formation is as follows:

   - A reactor into which aqueous carbamate solution is recycled, excess ammonia and carbon dioxide are fed.
   - A high-pressure separator where liquids and gases from the reactor are separated.
   - One or several steam-heated decomposers (or gas-swept strippers) where more gas-liquid separation occurs.
   - Several absorbers where gases from the decomposers and gas separator are absorbed into an aqueous stream that is recycled to the reactor.
   - An ammonia condenser that condenses and recycles to the reactor any ammonia gas that is not absorbed into the recycled aqueous stream.

   There is considerable difference in the carbamate solution recycle system from one plant to another.

2. Input Materials

   a. Once-through process (old plants)

      - 1.2 to 1.8 metric tons ammonia per metric ton urea.
      - 1.0 to 1.5 metric tons carbon dioxide per metric ton urea.

   b. Conventional recycle process

      - 0.57 metric tons ammonia per metric ton urea.
      - 0.76 metric tons carbon dioxide per metric ton urea.

3. Operating Parameters

   a. Once-through process (used only in old plants)

- Reactor temperature - 175 to 190°C.
- Reactor pressure - 200 kg/cm^2.
- Carbamate decomposer pressure - 2 kg/cm^2.
- Products - 85 to 90 weight percent aqueous urea solution.
  - gaseous NH_3, CO_2, H_2O mixture.

b. Conventional recycle process

- Reactor temperature - 185°C
- Reactor pressure - 200 kg/cm^2
- First stage decomposer pressure - 15 to 100 kg/cm^2
- Third (final) stage decomposer pressure - below atmospheric
- Product - 70 to 75 weight percent aqueous urea solution.

4. Utilities

- Electrical energy - 110 to 190 kWh per metric ton urea (assuming electric-driven compressor).
- Steam - 0.5 to 2 metric tons per metric ton urea.
- Cooling water - 60 to 130 cubic meters per metric ton urea.

5. Waste Streams - Condensate obtained by condensing the gases from the final decomposer is usually stripped of ammonia and discarded. The discarded condensate contains traces of ammonia.

6. EPA Classification Code - None exists.

7. References

Faith, W. L., D. B. Keyes, and R. L. Clark. Industrial Chemicals, 3rd Edition. New York, John Wiley & Sons, Inc., 1965. p. 790-795.

Green, R. V. Chapter 5. In: Reigel's Handbook of Industrial Chemistry, 7th Edition. Kent, J. A. (ed.). New York, Van Nostrand Reinhold Company, 1974. p. 104-111.

Mavrovic, I. Urea and Urea Derivatives. In: Kirk-Othmer Encyclopedia of Chemical Technology, 2nd Edition, Standen, A. (ed.). New York, John Wiley & Sons, Inc., 1970. 21:37-51.

Slack, A. V. Fertilizers. In: Kirk-Othmer Encyclopedia of Chemical Technology, 2nd Edition. Standen, A. (ed.). New York, John Wiley & Sons, Inc., 1966. 9:68-72.

Slack. A. V. Fertilizers. In: Kirk-Othmer Encyclopedia of Chemical Technology, 2nd Edition. Standen, A. (ed.). New York, John Wiley & Sons, Inc., 1971. Supplementary:343-351.

Urea Finishing

1. Function - This process (See Figure 4) produces urea prills from the aqueous urea solution forwarded from urea formation, Process 19. The urea prills are sold or used in making mixed fertilizers (Figure 7).

   Two different routes are used to reduce the urea solution to a molten state: evaporation and crystallization with crystal remelt. The resulting molten urea is solidified into small spherical particles called prills.

   Evaporation can be conducted under vacuum, under reduced pressure with the addition of hot air as a drying agent, or by a process of atmospheric air-sweep evaporation. In all cases, the urea solution is steam heated.

   A higher purity product results if the crystallization process is used. Crystals form in a vacuum crystallizer and the crystal slurry is sent to a continuous pusher type centrifuge. The urea crystals are separated from the mother liquor by centrifuging, washed with water, and dried. The mother liquor is recycled to the crystallizer. The urea crystals are elevated to the top of the prilling tower and melted in a steam-heated crystal melter.

   Molten urea from either process route is sprayed down a tower countercurrent to a stream of ambient temperature air. Spherical urea particles fall to the bottom of the prilling tower and are conveyed to a bulk storage or to bagging. Four-ply or six-ply polyethylene-coated paper bags are used in the bagging process. Prills may be coated with or may contain an anticaking agent.

2. Input Materials - 1.1 to 1.45 metric tons urea-water solution per metric ton urea prills.

3. Operating Parameters

   - Vacuum crystallizer.
     - Pressure - 0.08 kg/cm^2
     - Temperature - 60°C
   - Evaporation temperature - ~140°C (air swept evaporator).
   - Prilling tower - 50 meters tall.
   - Product using evaporation - 1.5 mm diameter prills containing 0.3 weight percent water and 0.7 weight percent biuret.
   - Product using crystallization - 1.5 mm diameter prills containing 0.2 weight percent water and 0.3 weight percent biuret.

4. Utilities

- Electrical energy - 5 kWh per metric ton urea.
- Steam - 0 to 0.5 metric tons per metric ton urea.
- Cooling water - 10 cubic meters per metric ton urea.

5. Waste Streams

- Water vapor from vacuum crystallizer or vacuum evaporators is condensed and discarded. It contains trace impurities (ammonia).
- Vapors from crystal drying may contain trace pollutants.
- Water vapor from air-swept evaporators contains trace impurities (ammonia).

6. EPA Classification Code - None exists.

7. References

Mavrovic, I. Urea and Urea Derivatives. In: Kirk-Othmer Encyclopedia of Chemical Technology, 2nd Edition. Standen, A. (ed.). New York, John Wiley & Sons, Inc., 1970. 21:51-52.

Slack, A. V. Fertilizers. In: Kirk-Othmer Encyclopedia of Chemical Technology, 2nd Edition. Standen, A. (ed.). New York, John Wiley & Sons, Inc., 1971. Supplement:351-352.

Ammonium Sulfate Formation

1. Function - This process (See Figure 4) produces ammonium sulfate crystals by reacting ammonia and sulfuric acid, crystallizing the resulting reaction product, and separating the crystals from water. The product can be sold or used in mixed and blended fertilizer manufacturing operations (Figure 7).

   Anhydrous ammonia is dissolved in water and fed along with a stream of sulfuric acid to a reactor. The resulting solution of ammonium sulfate is maintained at a pH of 3.5. It is pumped into double-effect crystallizers where water is evaporated under vacuum. Ammonium sulfate crystals form and grow until they are heavy enough to settle to the bottom of the crystallizer. A slurry containing the crystals is discharged into centrifuges where the crystals are spun dry, rinsed with water, and discharged onto a belt conveyor which carries the product to storage. The crystals are packaged in multiwall paper bags or sold in bulk.

   Much ammonium sulfate is produced as a by-product of coke manufacture in the steel industry and of caprolactam manufacture in the synthetic fiber industry.

2. Input Materials

   - 0.26 metric tons ammonia per metric ton ammonium sulfate.
   - 0.77 metric tons sulfuric acid (100% concentration) per metric ton ammonium sulfate.

3. Operating Parameters

   - Ammonia solution concentration - 18 to 26% solution
   - Slurry from crystallizers - 55 to 60% by volume crystals.
   - Crystal size
     - Standard - 70%; -16 mesh, +60 mesh
     - Large crystal - 80%; -10 mesh, +20 mesh
     - Granular - over 90%; -6 mesh, +16 mesh

4. Utilities

   - Electrical energy - 30 kWh per metric ton ammonium sulfate.
   - Water - 1 cubic meter per metric ton.

5. Waste Streams - Water vapor (1 metric ton per metric ton of product) is condensed and discarded.

6. EPA Classification Code - None exists.

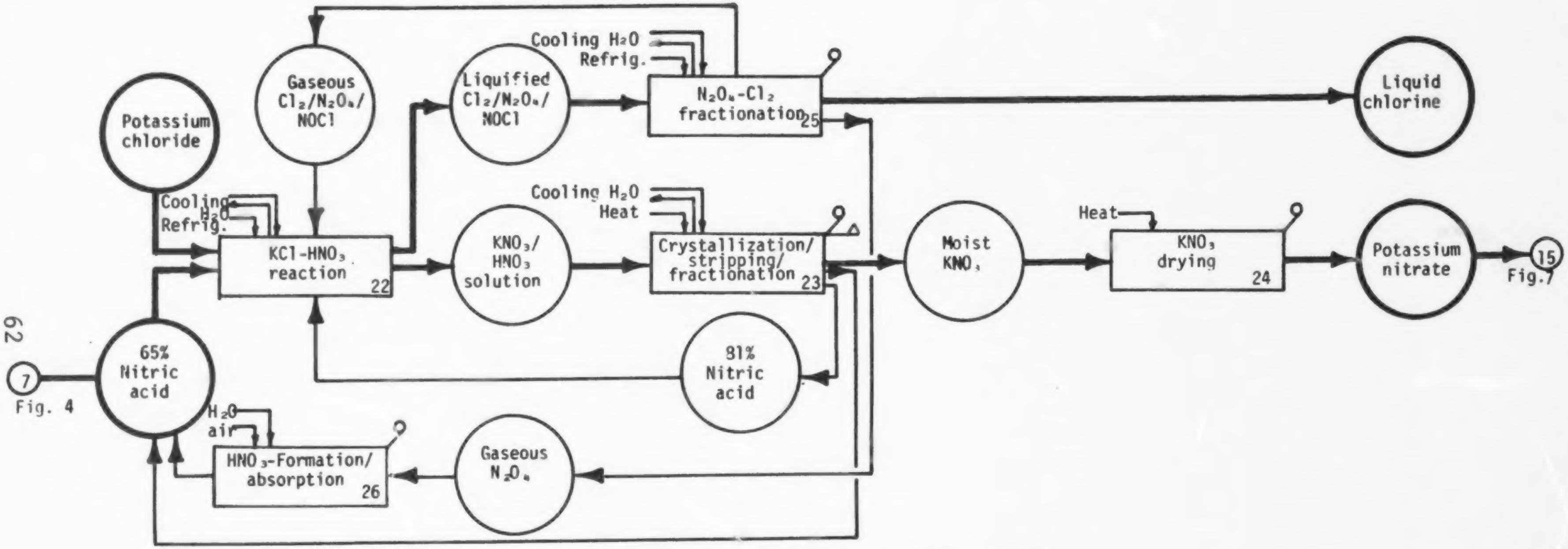
7. References

Faith, W. L., D. B. Keyes, and R. L. Clark. Industrial Chemicals, 3rd Edition. New York, John Wiley & Sons, Inc., 1965. p. 95-100.

Slack, A. V. Fertilizers. In: Kirk-Othmer Encyclopedia of Chemical Technology, 2nd Edition. Standen, A. (ed.). New York, John Wiley & Sons, Inc., 1966. 9:65-68.

PRODUCTION OF POTASSIUM NITRATE AND LIQUID CHLORINE

In this operation potassium chloride and nitric acid and their reaction products are combined in a series of processes to yield potassium nitrate as a product for fertilizer blending and liquid chlorine as a by-product.



Potassium chloride
Gaseous $Cl_2/N_2O_4/$ NOCl
Liquified $Cl_2/N_2O_4/$ NOCl
Cooling H_2O
Refrig.
N_2O_4-Cl_2 fractionation
25
Liquid chlorine
Cooling
H_2O
Refrig.
KCl-HNO_3 reaction
22
KNO_3/ HNO_3 solution
Cooling H_2O
Heat
Crystallization/ stripping/ fractionation
23
Moist KNO_3
Heat
KNO_3 drying
24
Potassium nitrate
15
Fig. 7
7
Fig. 4
65% Nitric acid
81% Nitric acid
H_2O
air
HNO_3-Formation/ absorption
26
Gaseous N_2O_4

Figure 5. POTASSIUM NITRATE AND LIQUID CHLORINE

KCl-HNO_3 Reaction

1. Function - This process (See Figure 5) receives potassium chloride (KCl), 65% nitric acid (HNO_3), and 81% HNO_3. It produces a potassium nitrate (KNO_3)/HNO_3 solution that is forwarded to crystallization/stripping/fractionation, Process 23. The process also produces a liquefied gas mixture that is forwarded to nitrogen tetroxide-chlorine fractionation, Process 25.

   Potassium chloride from storage is dissolved in cool 65% HNO_3 in a glass-lined vessel, and the solution fed to an agitated reaction tank along with some recycle 65% HNO_3 from HNO_3-formation absorption, Process 26, and crystallization/stripping/fractionation, Process 23. A reaction forms chlorine, KNO_3, nitrosyl chloride (NOCl) and water. Liquids from the reaction tank go to a muriate reaction column along with more recycled 65% HNO_3 where the reaction continues. Bottoms from this column consisting of a KNO_3/HNO_3 solution go to Process 23. Overhead from the muriate reaction column joins with vapors from the reaction tank plus a recycle gas stream from N_2O_4-Cl_2 fractionation, Process 25, and the combined vapors go to a gas reaction column. This column also is fed with recycled 81% HNO_3 from Process 23. A reaction between NOCl and HNO_3 forms nitrogen tetroxide (N_2O_4), more chlorine, and water in this column. Bottoms from the column are returned to the muriate reaction column. The overhead stream consisting of Cl_2, NOCl, nitryl chloride (NO_2Cl), bromine chloride (BrCl), and nitrogen tetroxide is liquefied by refrigeration and sent to Process 25. The BrCl comes from impurities in the KCl feed, and the NO_2Cl comes from side reactions.

2. Input Materials (per metric ton 95.4% purity KNO_3)

   - 1.01 metric tons fresh 65% HNO_3.
   - 0.74 metric tons KCl.
   - 2 to 5 metric tons recycle 65% HNO_3.
   - 1 to 3 metric tons recycle 81% HNO_3.

3. Operating Parameters

   - Pressure - 2.5 kg/cm^2.
   - Temperature range - 5°C to 130°C.
   - Muriate reaction column - 1.5 meters diameter x 12 meters tall with titanium cladding.
   - Gas reaction column - 1.5 meters diameter x 6 meters tall with glass lining.

4. Utilities

   - Electrical energy (primarily for refrigeration) - 50 kWh per metric ton 95.4% purity KNO_3.

- Cooling water - 30 cubic meters per metric ton 95.4% purity KNO_3.
- Steam - 1 metric ton per metric ton 95.4% purity KNO_3.

5. Waste Streams - None exists.

6. EPA Classification Code - None exists.

7. References

Haddeland, G. E. Potash Fertilizers. Report No. 14, Process Economics Program. Stanford Research Institute, Menlo Park, California. September 1966. 188 p.

Spealman, M. L. New Route to Chlorine and Saltpeter. Chemical Engineering. 72:198-200, November 8, 1965.

Crystallization/Stripping/Fractionation

1. Function - This process (See Figure 5) receives an aqueous potassium nitrate (KNO_3)/nitric acid (HNO_3) solution from KCl-HNO_3 reaction, Process 22, and produces moist KNO_3 crystals that are forwarded to KNO_3 drying, Process 24.

   Three separation techniques are required to remove most of the water and HNO_3 from the KNO_3. These techniques are distillation, vacuum crystallization, and centrifuging.

   The aqueous KNO_3/HNO_3 solution from Process 22 goes to a water stripping column. The bottoms from the column is a concentrated KNO_3/HNO_3 solution and it is fed to the first of three vacuum crystallizers. The slurry bottoms from the second and third crystallizers are sent to a centrifuge where moist KNO_3 crystals are separated from mother liquor. The crystals go to KNO_3 drying, Process 24. Other streams produced in this processing sequence are handled as follows.

   - The overhead water-rich stream from the water stripping column is forwarded to a water rectifier column. An 81% HNO_3 stream from the vacuum crystallizers also enters the water rectifier column. The bottoms from this column is 65% nitric acid which is used as feed to the KCl-HNO_3 reaction, Process 22. The overhead is water vapor which is condensed in a barometric condenser and discarded.

   - The vapor from the vacuum crystallizers is condensed. Its composition is 81% HNO_3. A portion of this stream is sent to the water rectifier column and the remainder is used in KCl-HNO_3 reaction, Process 22.

   - Mother liquor from the centrifuge is recycled to the vacuum crystallizers.

   - The bottoms slurry from the first vacuum crystallizer is recycled to the water stripper column. This increases the KNO_3 concentration in the column and results in a stronger HNO_3 vapor from the vacuum crystallizers. This high strength (81% HNO_3) acid is needed in Process 22.

2. Input Materials - 5 metric tons of KNO_3/HNO_3 solution per metric ton of 95.4% purity KNO_3.

3. Operating Parameters

   - Water stripping column
     - Pressure - Below atmospheric.

Temperature - Overhead stream is below 100°C.
Feed is approximately 20% KNO_3, 44% HNO_3, 36% water plus minor amounts of KCl, NaCl, $NaNO_3$, $MgCl_2$, HCl, and other metal nitrates.

- Water rectifier column
  Pressure - below atmospheric, probably ~0.1 kg/cm^2.
  Temperature of overhead is approximately 40°C.
- Vacuum crystallizers
  Temperature range - 35°C to 110°C.
  Pressure range - 0.05 to 0.5 kg/cm^2
- Centrifuge
  Basket size - 1 meter long.
- Plant size - 57,000 metric tons of 95.4% purity KNO_3 per year.

4. Utilities

- Steam - 2 metric tons per metric ton of 95.4% purity KNO_3.
- Electrical energy - 30 kWh per metric ton of 95.4% purity KNO_3.
- Cooling water - 100 cubic meters per metric ton of 95.4% purity KNO_3.

5. Waste Streams

- Some vapors from the water rectifier column are not condensed in the barometric condenser. These vapors are released to the atmosphere. They contain some HNO_3.

- The overhead stream from the water rectifier column is condensed in a barometric condenser. This water is discarded. It amounts to approximately 0.5 cubic meters per metric ton 95.4% purity KNO_3 produced. It contains some HNO_3.

6. EPA Classification Code - None exists.

7. References

Haddeland, G. D. Potash Fertilizers. Report No. 14, Process Economics Program. Stanford Research Institute, Menlo Park, California, September 1966. 188 p.

Spealman, M. L. New Route to Chlorine and Saltpeter. Chemical Engineering. 72:198-200, November 8, 1965.

KNO_3 Drying

1. Function - This process (See Figure 5) receives moist KNO_3 crystals from crystallization/stripping/fractionation, Process 23 and dries them. The resulting granular or prilled product is used in producing blended fertilizers, Figure 7.

   A direct-fired or steam-heated rotary dryer is used to dry the KNO_3. An anticaking agent may be added to the dry, granular KNO_3 exiting the dryer.

   If a prilled product is desired, the dry, granular KNO_3 from the dryer is remelted and sprayed down into a prilling tower countercurrent to upward moving air. The prills are removed from the bottom of the tower, cooled in a rotary cooler, and conveyed to storage.

2. Input Materials - 1.02 metric tons moist KNO_3 per metric ton 95.4% purity potassium nitrate.

3. Operating Parameters

   - Rotary direct-fired dryer - 2.5 meters diameter x 12 meters long with titanium cladding.
   - Temperature - 200°C.
   - Pressure - Atmospheric

4. Utilities

   - Steam - 0.1 to 0.3 metric ton per metric ton 95.4% purity potassium nitrate.
   - Electrical energy - 2 kWh per metric ton 95.4% purity potassium nitrate.

5. Waste Streams - Hot air from the rotary dryer contains nitrogen oxides from the moist potassium nitrate feed. An estimate of the quantity is 0.02 metric tons per metric ton of 95.4% purity potassium nitrate produced. Particulates are also present in the exiting air.

6. EPA Classification Code - None exists.

7. References

Haddeland, G. E. Potash Fertilizers. Report No. 14, Process Economics Program. Stanford Research Institute, Menlo Park, California, September 1966. 188 p.

Spealman, M. L. New Route to Chlorine and Saltpeter. Chemical Engineering. 72:198-200, November 8, 1965.

N_2O_4-Cl_2 Fractionation

1. Function - This process (See Figure 5) receives a stream of liquefied mixed gases from KCl-HNO_3 reaction, Process 22, and separates it into liquid chlorine product, a mixed gas stream that is recycled to Process 22, and a liquid nitrogen tetroxide stream that is forwarded to HNO_3 Formation/Absorption, Process 26.

   Liquefied mixed gases [chlorine (Cl_2), nitrosylchloride (NOCl), nitryl chloride (NO_2Cl), bromine chloride (BrCl), and nitrogen tetroxide (N_2O_4)] are received from Process 22 and fed to a chlorine fractionating column. Liquid, 99.5% purity chlorine is the overhead product. The bottoms stream is sent to a second fractionating column. The overhead from the second column is a mixture of NOCl, NO_2Cl, N_2O_4, Cl_2, and BrCl gases which is recycled to Process 22. The bottoms is 99.5% purity nitrogen tetroxide. It is forwarded to Process 26.

2. Input Materials - 0.8 metric tons liquefied mixed gases per metric ton of 95.4% purity KNO_3.

3. Operating Parameters

   - Plant size - 57,000 metric tons of 95.4% purity KNO_3 per year.
   - Chlorine fractionating column.
     1 meter diameter x 8 meters tall with monel and tantalum cladding.
     Temperature range in column - minus 10°C to 40°C.
     Pressure - 2.5 kg/cm^2.
     Chlorine product - 0.35 metric tons per metric ton 95.4% purity KNO_3.
   - Nitrogen tetroxide column.
     0.6 meters diameter x 8 meters tall with 347 stainless steel cladding.
     Temperature range in column - 0°C to 40°C.
     Pressure - 2.5 kg/cm^2.

4. Utilities

   - Electrical energy (primarily for refrigeration) - 40 kWh per metric ton 95.4% purity KNO_3.
   - Cooling water - 10 cubic meters per metric ton 95.4% purity KNO_3.
   - Steam - 0.1 metric ton per metric ton 95.4% purity KNO_3.

5. Waste Streams - A bleed off the nitrogen tetroxide fractionation column overhead stream is sent to a gas scrubber. Traces of BrCl, Cl_2, N_2O_4, NOCl, and NO_2Cl may be released to the atmosphere from this scrubber.

6. EPA Classification Code - None exists.

7. References

Haddeland, G. E. Potash Fertilizers. Report No. 14, Process Economics Program. Stanford Research Institute, Menlo Park, California. September 1966. 188 p.

Spealman, M. L. New Route to Chlorine and Saltpeter. Chemical Engineering. 72:198-200, November 8, 1965.

HNO_3-Formation/Absorption

1. Function - This process (See Figure 5) receives liquid nitrogen tetroxide (N_2O_4) from N_2O_4-Cl_2 fractionation, Process 25, and produces 65% nitric acid which is used as feed to KCl-HNO_3 reaction, Process 22.

   Liquid N_2O_4 is combined with 55% HNO_3 and air in an agitated vessel to form more nitric acid. Liquid from the mixing vessel goes to a series of two absorption towers. In the first (primary), it passes countercurrent to a gaseous mixture of vapors from the mixing tank and from the other absorption tower. In the second tower, the liquid passes countercurrent to air. The liquid product from the second tower is 65% nitric acid. The gaseous vapors exiting the absorption system are scrubbed with a water stream fed to the top of the primary tower, and then they are vented to the atmosphere.

2. Input Materials

   - 0.45 metric tons 99.5% purity N_2O_4 per metric ton 95.4% purity KNO_3.
   - 0.8 to 2 metric tons 55% nitric acid per metric ton 95.4% purity KNO_3.
   - 0.4 metric tons air per metric ton 95.4% purity KNO_3.
   - 0.1 to 0.3 metric tons water per metric ton 95.4% purity KNO_3.

3. Operating Parameters

   - Pressure - 8 kg/cm^2.
   - Temperature - ~40°C.

4. Utilities - Electrical energy - 60 kWh per metric ton 95.4% purity KNO_3.

5. Waste Streams - Vapors from the reaction-absorption system are vented to the atmosphere. These vapors amount to 0.3 metric tons per metric ton 95.4% purity KNO_3. The stream is primarily nitrogen, but contains traces of nitrogen oxides.

6. EPA Classification Code - None exists.

7. References

Haddeland, G. E. Potash Fertilizers. Report No. 14, Process Economics Program. Stanford Research Institute, Menlo Park, California. September 1966. 188 p.

Spealman, M. L. New Route to Chlorine and Saltpeter. Chemical Engineering. 72:198-200, November 8, 1965.

PRODUCTION OF AMMONIUM PHOSPHATES AND NITRIC PHOSPHATE

The processes in this group combine phosphoric acid and in some cases nitric or sulfuric acid with ammonia or with phosphate rock and ammonia to produce four different ammonium phosphates and nitric phosphate. These materials are used in blending mixed fertilizers.

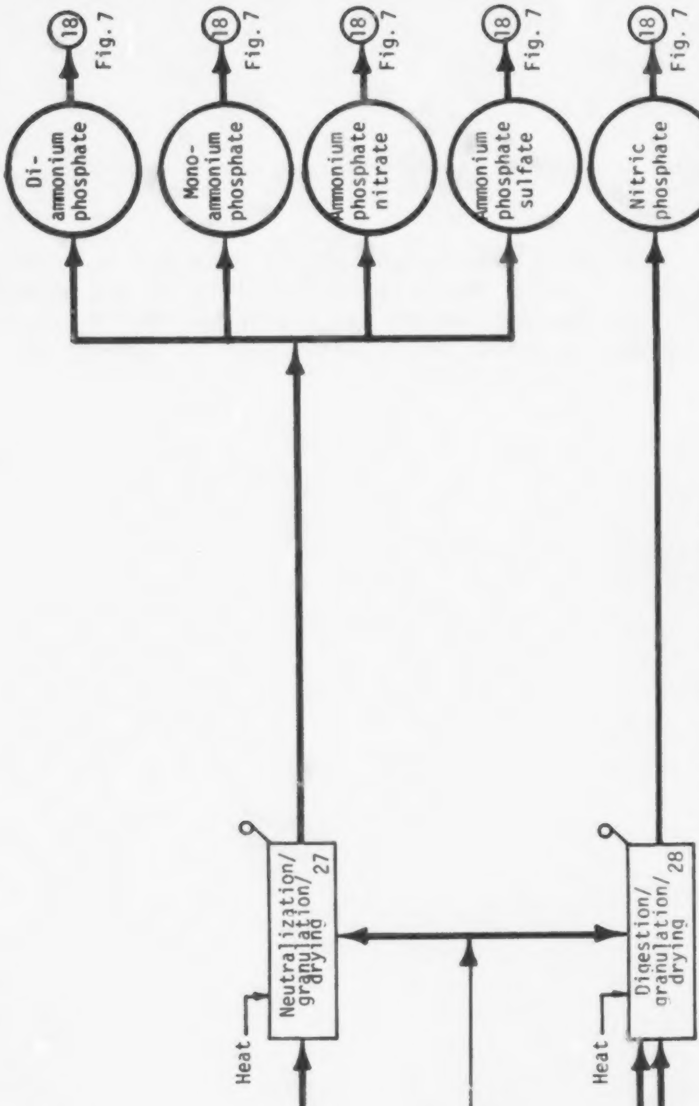


Fig. 2
2
16
Fig. 3
Phosphoric acid
12
Fig. 2
Sulfuric acid
7
Fig. 4
Nitric acid
1
Fig. 2
Phosphate rock
6
Fig. 3
Anhydrous ammonia
Heat
Neutralization/ granulation/ drying
27
Heat
Digestion/ granulation/ drying
28
Di- ammonium phosphate
Mono- ammonium phosphate
Ammonium phosphate nitrate
Ammonium phosphate sulfate
Nitric phosphate
18
Fig. 7
18
Fig. 7
18
Fig. 7
18
Fig. 7
18
Fig. 7

Figure 6. AMMONIUM PHOSPHATES AND NITRIC PHOSPHATE

Neutralization/Granulation/Drying

1. Function - This process (See Figure 6) reacts anhydrous ammonia with phosphoric acid or with phosphoric and sulfuric (or nitric) acid to obtain a slurry product. The slurry is then granulated and dried.

   The neutralization reaction can be started in a preneutralizer tank and finished in a rotary drum granulator where ammonia is injected into the slurry bed. Another arrangement is to allow the neutralization reaction to go to completion in a series of tanks before feeding the product slurry to a blunger. A third arrangement is to feed phosphoric acid onto a bed of recycled product fines in a rotary drum granulator and to inject ammonia under the bed of fines. In this third arrangement neutralization and granulation occur in the same piece of equipment. Heat of ammoniation evaporates water in all of these arrangements.

   Product from the rotary drum or blunger granulator is fed to a dryer and then to screens. Fines are recycled to the granulator, oversize is fed to a crusher and either recycled to the screens or to the granulator, and onsize material is conveyed to storage.

2. Input Materials

   - Anhydrous ammonia - 0.14 metric tons per metric ton ammonium phosphate product or 0.23 metric tons per metric ton diammonium phosphate product or 0.13 to 0.3 metric tons per metric ton of ammonium phosphate sulfate or ammonium phosphate nitrate product depending on the product.
   - Phosphoric acid (75% acid basis) - 0.54 cubic meters per metric ton of ammonium or diammonium phosphate products or 0.1 to 0.54 cubic meters per metric ton of ammonium phosphate sulfate or ammonium phosphate nitrate product depending on the product.
   - Sulfuric acid (100% acid basis) - 0.03 to 0.25 cubic meters per metric ton of ammonium phosphate sulfate product depending on product.
   - Nitric acid (100% acid basis) - 0.1 to 0.4 cubic meters per metric ton of ammonium phosphate nitrate product depending on product.

3. Operating Parameters

   - Temperature rises to 90 to 110°C in the preneutralizer, granulator, or ammoniation tank due to the heat of reaction.
   - Typical plant capacity - 10 to 40 metric tons per year of 18-46-0 fertilizer (diammonium phosphate).
   - Recycle ratio of fines to fresh feed in the granulator ranges from less than 2:1 to more than 8:1.

- Granulator size - 1.5 to 3.5 meters diameter x 2 to 8 meters long.
- Product size - 6 to 20 mesh.

4. Utilities

- Electrical energy - 20 kWh per metric ton product.
- Fuel for drying - 125,000 kcal per metric ton product.

5. Waste Streams - Scrubbers are used to decrease ammonia emissions from the ammoniation tank and/or granulator. Incoming phosphoric acid can be used as the scrubbing fluid. No quantitative data on emissions are available. A gross estimate is that 5 percent of the ammonia or from 0.005 to 0.01 metric ton ammonia per metric ton of product is emitted to the atmosphere.

6. EPA Classification Code

3-01-030-01	Dryer-Coolers
3-01-030-02	Amoniat-Granulate

7. References

Slack, A. V. Fertilizers. In: Kirk-Othmer Encyclopedia of Chemical Technology, 2nd Edition. Standen, A. (ed.). New York, John Wiley & Sons, Inc., 1966. 9:125-132.

Snow, R. H. Size Reduction and Size Enlargement. In: Chemical Engineers' Handbook, 5th Edition. Perry, R. H., and C. H. Chilton (eds.). New York, McGraw-Hill Book Company, 1973. p. 8-62 to 8-63.

Digestion/Granulation/Drying

1. Function - This process (See Figure 6) dissolves phosphate rock in nitric acid (or nitric acid plus sulfuric acid and/or phosphoric acid), neutralizes the resulting slurry with anhydrous ammonia, granulates, and dries the product.

   Normally, rock acidulation is carried out in two or three vessels, followed by up to twelve tanks for ammoniation. The ammoniated slurry is granulated in equipment such as pugmills, rotary drums, and the spherodizer. A rotary dryer is used to dry the slurry product. Screening separates the granules into undersize fines which are returned to the granulator, oversize material which is crushed and either recycled to the granulator or the screens, and onsize material which is conveyed to storage.

2. Input Materials - (approximate)

   - Phosphate rock - 0.35 metric ton per metric ton nitric phosphate product.
   - Phosphoric acid (75% basis) - 0.12 cubic meters per metric ton nitric phosphate product.
   - Nitric acid (100% basis) - 0.28 cubic meters per metric ton nitric phosphate product.
   - Sulfuric acid (100% basis) - 0 to 0.1 cubic meters per metric ton nitric phosphate product.
   - Anhydrous ammonia - 0.12 metric tons per metric ton nitric phosphate product.

3. Operating Parameters

   - Acidulation tanks - temperature rises to 60°C.
   - Temperature rises to 90 to 110°C in the ammoniation tanks.
   - Recycle ratio of fines to fresh feed in the granulator ranges from less than 2:1 to more than 8:1.
   - Granulator size - 1.5 to 3.5 meters diameter x 2 to 8 meters long
   - Product size - 6 to 20 mesh.
   - Fluorine-containing off-gases are scrubbed with water.

4. Utilities

   - Electrical energy - 20 kWh per metric ton nitric phosphate product.
   - Fuel for drying - 125,000 kcal per metric ton nitric phosphate product.

5. Waste Streams - Scrubbers are used to decrease ammonia emissions from the ammoniation tanks and/or granulator. Incoming nitric acid can be used as the scrubbing fluid. A gross estimate of ammonia emissions is 0.001 to 0.01 metric tons per metric ton of nitric phosphate product.

Effluent scrubber water, containing HF and H_2SiF_6 is run into beds of limestone to precipitate CaF_2. The latter is considered to be solid waste. Information was not available on the efficiency of scrubbers in removing gaseous contaminants.

6. EPA Classification Code - None exists.

7. References

Slack, A. V. Fertilizers. In: Kirk-Othmer Encyclopedia of Chemical Technology, 2nd Edition. Standen, A. (ed.). New York, John Wiley & Sons, Inc., 1966. 9:132-135.

Snow, R. H. Size Reduction and Size Enlargement. In: Chemical Engineers' Handbook, 5th Edition. Perry, R. H., and C. H. Chilton (eds.). New York, McGraw-Hill Book Company, 1973. p. 8-62 to 8-63.

PRODUCTION OF MIXED FERTILIZERS

The processes in this operation are often carried out in relatively small plants near the point of application of the fertilizer rather than near raw materials.

Intermediate materials produced by other segments of the industry are dissolved and reacted or blended by mixing dry materials together to produce mixed fertilizers of varying compositions to suit localized needs.

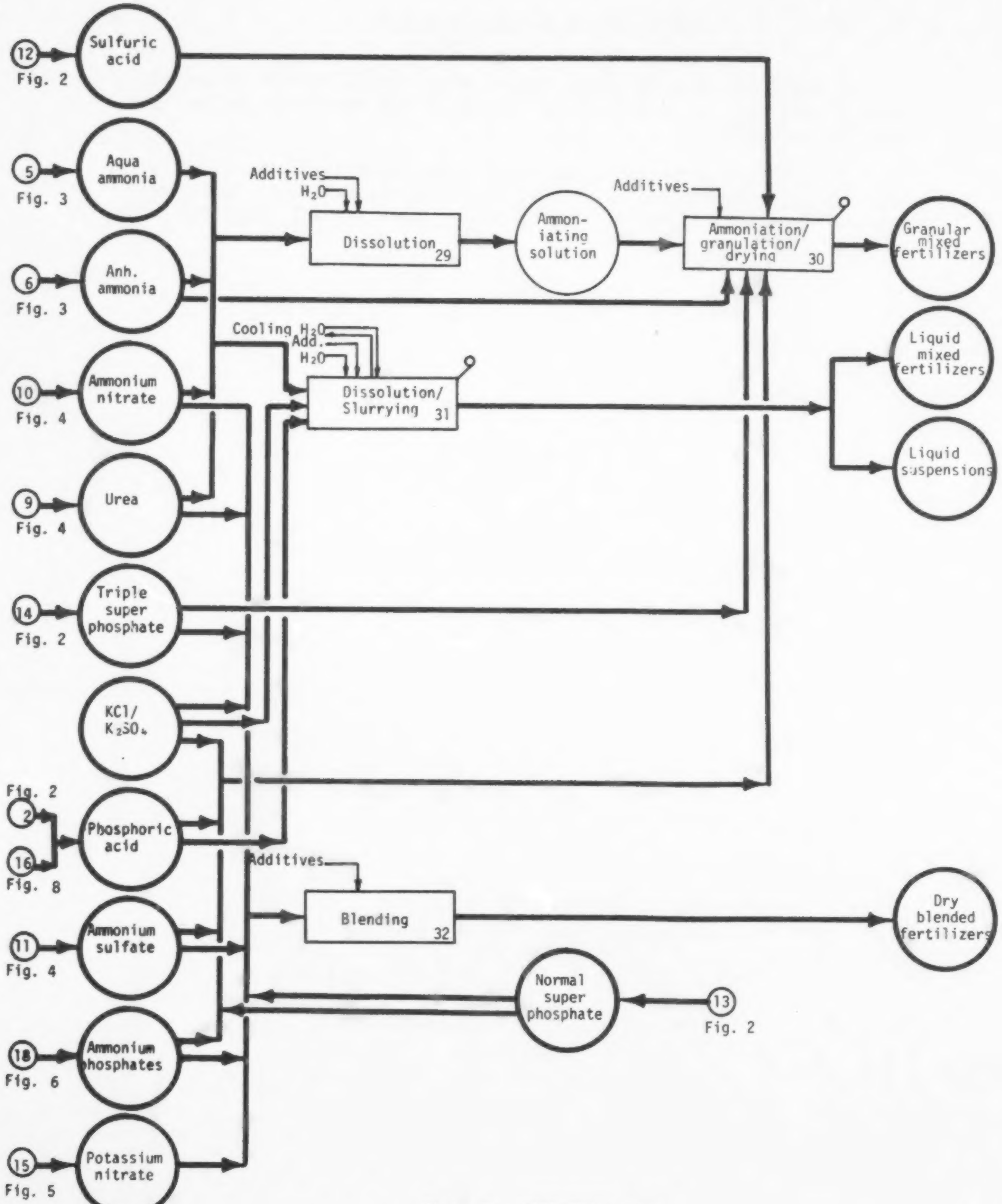

12
Fig. 2
Sulfuric acid
5
Fig. 3
Aqua ammonia
6
Fig. 3
Anh. ammonia
10
Fig. 4
Ammonium nitrate
9
Fig. 4
Urea
14
Fig. 2
Triple super phosphate
KCl/ K_2SO_4
Fig. 2
2
16
Fig. 8
Phosphoric acid
11
Fig. 4
Ammonium sulfate
18
Fig. 6
Ammonium phosphates
15
Fig. 5
Potassium nitrate
Additives
H_2O
Dissolution 29
Ammon- iating solution
Additives
Ammoniation/ granulation/ drying 30
Granular mixed fertilizers
Cooling H_2O
Add.
H_2O
Dissolution/ Slurrying 31
Liquid mixed fertilizers
Liquid suspensions
Additives
Blending 32
Dry blended fertilizers
Normal super phosphate
13
Fig. 2

Figure 7. MIXED FERTILIZERS

Dissolution

1. Function - This process (See Figure 7) forms an ammoniating solution by combining aqua ammonia, anhydrous ammonia, ammonium nitrate, and/or urea with water. The resulting solution goes to ammoniation/granulation/drying, Process 30. Additives containing secondary- and micronutrients may be included in the ammoniating solution. In some instances, anhydrous ammonia is fed to Process 30 and Process 29 is by-passed.

2. Input Materials

   Selected solutions:

   - Anhydrous ammonia - up to 0.15 cubic meters per metric ton granular mixed fertilizer.
   - Ammonium nitrate - up to 0.2 metric tons per metric ton granular mixed fertilizer.
   - Urea - up to 0.06 metric tons per metric ton granular mixed fertilizer.
   - Water - up to 0.06 cubic meters per metric ton granular mixed fertilizer.

3. Operating Parameters

   - Atmospheric pressure.
   - Typically 30 to 40 °C.
   - Solution vapor pressure - 0.05 to 7 kg/cm^2 at 40°C.
   - Water content - 0.5 to 18 percent.
   - Solution crystallization temperature - from below minus 40°C to 17°C.
   - Nitrogen content :37 to 53 percent.
   - Ratio of fixed N to free N - 0.3 to 3.0.
   - Typical solution compositions:
     - Anhydrous ammonia (11 to 49 percent)
     - Ammonium nitrate (36 to 66 percent)
     - Urea (up to 19 percent)
     - Water (up to 18 percent)

4. Utilities - Electrical energy - <0.1 kWh per metric ton granular mixed fertilizer.

5. Waste Streams - None exists.

6. EPA Specification Code - None exists.

7. References

Hardesty, J. Q., and L. B. Hein. Chapter 18. In: Riegel's Handbook of Industrial Chemistry, 7th Edition. Kent, J. A. (ed.). New York, Van Nostrand Reinhold Company, 1974. p. 559.

Slack, A. V. Fertilizers. In: Kirk-Othmer Encyclopedia of Chemical Technology, 2nd Edition. Standen, A. (ed.). New York, John Wiley & Sons, Inc., 1966. 9:114-122.

Ammoniation/Granulation/Drying

1. Function - This process (See Figure 7) first reacts anhydrous ammonia or the ammoniating solution from Process 29 with superphosphate and possibly potash and/or ammonium sulfate or ammonium phosphate. Sulfuric or phosphoric acid is also included in the formulation to fix excess ammonia. The solid reaction product is screened to obtain a desirable size fraction and the product may be dried before conveying to storage. Additives containing secondary and micronutrients may be included in these formulations.

   Ammoniation and granulation can be carried out in the same vessel. However, the ammoniating solution and the acids are often reacted in a preneutralization tank. Then the liquids and solid materials are mixed in a granulation vessel which is usually a twin-shaft pugmill or a rotary drum. Both ammonia and acid may be sparged into the granulator under the solids. The solids leaving the granulator are screened. Fines are recycled to the granulator while oversize particles are crushed and either rescreened or recycled. Properly sized product may be dried in rotary driers if it requires drying. It is then cooled and conveyed to storage.

2. Input Materials - (per metric ton granular mixed fertilizer)

   •Ammoniating solution - up to 0.3 cubic meters

   •Anhydrous ammonia - up to 0.1 cubic meters.

   •Super phosphate
      Normal - 0.15 to 0.45 metric tons.
      Triple - up to 0.35 metric tons.
   •Ammonium sulfate - up to 0.2 metric tons.
   •Diammonium phosphate - up to 0.15 metric tons.
   •Potassium chloride - up to 0.35 metric tons.
   •Sulfuric acid (100% basis) - up to 0.04 cubic meters
   •Phosphoric acid (75% H_3PO_4)- up to 0.15 cubic meters.

3. Operating Parameters

   •Particle size of superphosphate - preferably 40 to 80 mesh.
   •Temperature reaches 30 to 110°C either in the granulator or in the preneutralizer due to the heat of reaction.
   •Granulator size - 1.5 to 3.5 meters diameter x 2 to 8 meters long.
   •Granulator production capacity - 10 to 40 metric tons product per hour.
   •Granulator power requirement - 20 to 80 kW.

- Retention time in granulator - 1 to 2 minutes.
- Product size - 6 to 20 mesh.
- Product moisture content - <1 percent for high-nitrogen grades and <3 percent for a low-nitrogen product.
- Recycle ratio of fines to fresh slurry in the granulator ranges from 1:1 to 6:1.

4. Utilities

- Electrical energy - 20 kWh per metric ton granular mixed fertilizer.
- Fuel for drying - up to 100,000 kcal per metric ton granular mixed fertilizer.

5. Waste Streams - Ammonia losses may occur from the granulator. The use of incoming phosphoric acid or sulfuric acid to scrub vapors from the granulator should eliminate most of this emission. No quantitative data are available. A gross estimate is that from 0.001 to 0.01 metric ton ammonia is emitted per metric ton granular mixed fertilizer product.

6. EPA Classification Code - None exists.

7. References

Hardesty, J. Q., and L. B. Hein. Chapter 18. In: Riegel's Handbook of Industrial Chemistry, 7th Edition. Kent, J. A. (ed.). New York, Van Nostrand Reinhold Company, 1974. p. 558-565.

Slack, A. V. Fertilizers. In: Kirk-Othmer Encyclopedia of Chemical Technology, 2nd Edition. Standen, A. (ed.). New York, John Wiley & Sons, Inc., 1966. 9:114-125.

Snow, R. H. Size Reduction and Size Enlargement. In: Chemical Engineers' Handbook, 5th Edition. Perry, R. H., and C. H. Chilton (eds.). New York, McGraw-Hill Book Company, 1973. p. 8-62 to 8-63.

Dissolution/Slurrying

1. Function - This process (See Figure 7) forms an ammonium phosphate solution containing other fertilizer materials. The primary ingredients of the liquid product are ammonia and phosphoric acid. Other materials often included are urea, ammonium nitrate, potash, polyphosphates, and superphosphoric acid. Additives containing secondary and micronutrients may be included in these formulations.

   "Hot-mix" liquid fertilizer plants consist of storage tanks, a reactor tank, and cooler. Water, then the other liquids, and then batch weighed potash are fed into the reactor tank. The resulting solution is then cooled to remove the heat of reaction.

   "Cold-mix" plants consist only of storage tanks and a mix-weigh tank. The phosphate is supplied as a neutral solution (mixture of ammonium phosphates) often from "hot-mix" plants.

   Slurry fertilizers containing more potash--as well as other salts in some formulations--than the liquid fertilizers are also made. The salts are carried in suspension as finely divided crystals. A suspending agent (usually attapulgite clay) is used to thicken the suspension, reduce settling and inhibit crystal growth.

2. Input Materials

   - Phosphoric acid
   - Ammonia
   - Urea
   - Ammonium nitrate
   - Potash
   - Polyphosphate
   - Superphosphoric acid
   - Water

   Varying amounts of the above ingredients are used to produce a wide range of formulations. Usually electric furnace phosphoric acid is used because of its high purity. If wet process phosphoric acid is used, superphosphoric acid or a polyphosphate solution is included in the formulation to sequester impurities and hold them in solution. Ten to forty percent of the phosphate in the formulation may be supplied by these additives. However, polyphosphates are sometimes used as the sole source of phosphate in liquid fertilizer formulations.

3. Operating Parameters

   - 1 to 3 percent attapulgite clay in slurry mixed fertilizer.

- Typical slurry mixed fertilizers - 15-15-15,* 10-30-10, 20-20-0.
- Crystallization temperature of liquid mixed fertilizers is usually below 0°C.
- Typical products from "hot-mix" plants (feed to "cold mix" plants) - 8-24-0, 10-34-0, 11-37-0, 4-11-11.
- Typical "hot-mix" batch - 15 metric tons in 45 minutes.
- Typical feeds to "cold-mix" plants - 10-34-0, 4-11-11, nitrogen solution contain urea and ammonium nitrate.

4. Utilities

- Electrical energy - less than 1 kWh per metric ton liquid mixed fertilizer.
- Cooling water (hot mix plant) - 5 cubic meters per metric ton of liquid mixed fertilizer.
- Temperature - may reach 60 to 80°C in "hot-mix" plant.

5. Waste Streams - Some ammonia may be released in the "hot-mix" method of making liquid mixed fertilizers. No quantitative emissions data are available.

6. EPA Classification Code - None exists.

7. References

Hardesty, J. Q., and L. B. Hein. Chapter 18. In: Riegel's Handbook of Industrial Chemistry, 7th Edition. Kent, J. A. (ed.). New York, Van Nostrand Reinhold Company, 1974. p. 565-566.

Slack, A. V. Fertilizers. In: Kirk-Othmer Encyclopedia of Chemical Technology, 2nd Edition. Standen, A. (ed.). New York, John Wiley & Sons, Inc., 1966. 9:135-140.

---

* A long established practice of the industry is to designate the guaranteed minimum plant-nutrient content of fertilizer materials by a series of numerals separated by hyphens. These refer respectively to the contained percentages of nitrogen, P_2O_5, and K_2O. Thus 12-20-10 designates a fertilizer containing 12% nitrogen, 20% P_2O_5 and 10% K_2O.

Bulk Blending

1. Function - This process (See Figure 7) produces a large number of fertilizer blends by mixing various amounts of basic fertilizer materials. Additives containing secondary and micronutrients may also be included in the formulations.

   Granular raw materials are fed from storage lines to a mixer using screw feeders or belt conveyors. The mixers are mainly of the rotating-drum type, but other types such as ribbon mixers, mixing screws, and gravity mixing towers are used. After mixing, the blend is dropped into hoppers, bins, or vehicles.

2. Input Materials

   - Ammonium nitrate
   - Ammonium sulfate
   - Normal superphosphate
   - Triple superphosphate
   - Potassium chloride
   - Potassium sulfate
   - Urea
   - Ammonium phosphates (ammonium phosphate, diammonium phosphate, ammonium phosphate nitrate, ammonium phosphate sulfate).
   - Potassium nitrate

   Many combinations of the above materials can be used.

   Minor percentages (<1 percent) of magnesium, zinc, copper, molybdenum, and boron salts can also be blended into the fertilizer blends.

3. Operating Parameters

   - Raw material size uniformity is important. Particle size should be minus 6-, plus 16-mesh.
   - Storage, conveying, and mixing facilities vary widely and tend to be homemade.
   - Batch type mixing.
   - Usual batch size - 1 to 2 metric tons.
   - Mixing time - 2 to 3 minutes.

4. Utilities - Electrical energy - <1 kWh per metric ton blended fertilizer.

5. Waste Streams - Because the fertilizers contain moisture, there are no dust emissions.

6. EPA Classification Code - None exists.

7. References

Hardesty, J. Q., and L. B. Hein. Chapter 18. In: Riegel's Handbook of Industrial Chemistry, 7th Edition. Kent, J. A. (ed.). New York, Van Nostrand Reinhold Company, 1974. p. 565.

Slack, A. V. Fertilizers. In: Kirk-Othmer Encyclopedia of Chemical Technology, 2nd Edition. Standen, A. (ed.). New York, John Wiley and Sons, Inc., 1966. 9:140-143.

ELEMENTAL PHOSPHORUS AND FURNACE ACID SEGMENT

SEGMENT DESCRIPTION

The companies competing in the segment produce a group of end products derived from the electric furnace process for producing elemental phosphorus. The end-product group includes a considerable tonnage of material whose end use is unrelated to fertilizers. Estimated total production capacity of the segment in 1974 was between 1.5 and 2.5 million metric tons of P_2O_5 equivalent, including elemental phosphorus.

Companies in this segment include those that have used furnace acid as a source of high grade phosphoric acid for the production of sodium phosphates and calcium phosphates. Use of these phosphates for human consumption necessitates the use of a more purified form of phosphoric acid than is directly available as industrial wet process acid. Production or purchase of furnace acid has historically been less expensive than production and subsequent purification of wet process acid.

The ultimate primary raw material of the segment is phosphate rock or phosphate rock concentrates from which gaseous elemental phosphorus is directly obtained in the electric furnace process. An advantage of this process is that it is able to use low grade phosphate rock that is unsuitable for the rest of the industry; however, operation of the electric furnance results in the segment's relatively large consumption of electrical energy. Estimated electric power consumption capacity in 1974 for elemental phosphorus alone amounted to more than 700 MW.

Eleven companies have enterprises inside the segment in approximately 30 facilities. Most of the companies are large corporations producing other industry products outside the segment and also non-industry products.

The segment experienced a negative growth rate during the past five years as a result of the limits imposed on the phosphate content of detergents. The decline has been accentuated recently by the impact of energy costs on electric furnace operations. Some sources predict the early disappearance of furnace acid, supplanted by purified wet-process acid, with elemental phosphorus produced only for non-industry consumption.

Industry end products include elemental phosphorus, furnace acid, sodium phosphates, calcium phosphates and ferro-phosphorus. Furnace slag is a by-product or a waste material if no market exists. All segment products are indicated on the industry end product list appearing in Appendix B.

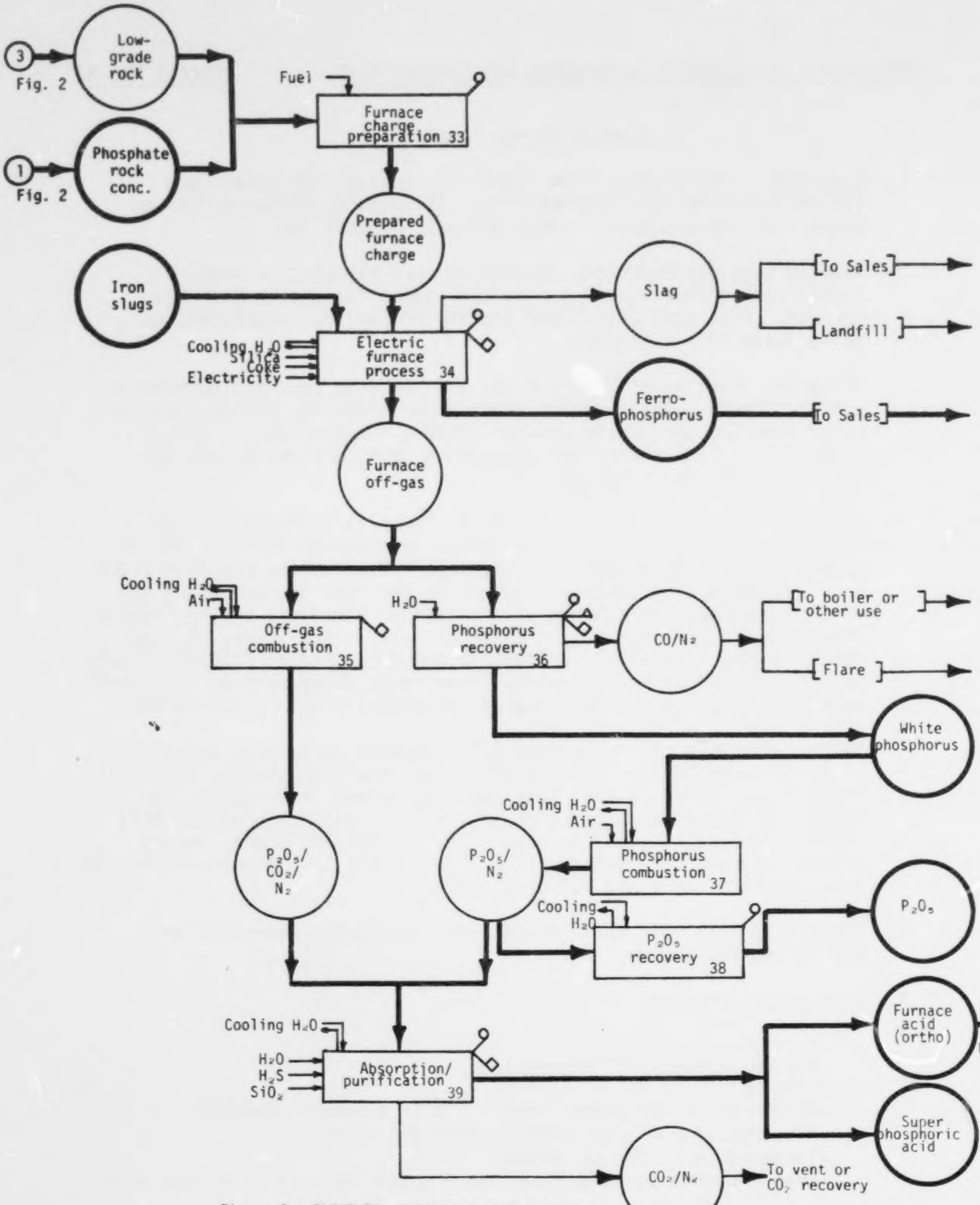
Segment operations are diagrammed on the final two flow sheets, Figures 8 and 9.

PRODUCTION OF ELEMENTAL PHOSPHORUS AND FURNACE ACID

The processes in this operation convert phosphate rock and iron slugs to elemental phosphorus, phosphorus pentoxide, orthophosphoric acid (furnace acid), superphosphoric acid and ferrophosphorus.

Treatment and disposal of water from phosphorus recovery is one of the major environmental concerns of the industry.

This operation belongs to the Elemental Phosphorus and Furnace Acid Segment of the industry.



3
Fig. 2
Low-grade rock
1
Fig. 2
Phosphate rock conc.
Fuel
Furnace charge preparation 33
Prepared furnace charge
Iron slugs
Cooling H_2O
Silica
Coke
Electricity
Electric furnace process 34
Slag
To Sales
Landfill
Ferro-phosphorus
To Sales
Furnace off-gas
Cooling H_2O
Air
Off-gas combustion 35
H_2O
Phosphorus recovery 36
CO/N_2
To boiler or other use
Flare
White phosphorus
Cooling H_2O
Air
Phosphorus combustion 37
$P_2O_5/CO_2/N_2$
P_2O_5/N_2
Cooling H_2O
P_2O_5 recovery 38
P_2O_5
Cooling H_2O
H_2O
H_2S
SiO_2
Absorption/ purification 39
Furnace acid (ortho)
16
Figs. 6, 7, 9
Super phosphoric acid
CO_2/N_2
To vent or CO_2 recovery

Figure 8. ELEMENTAL PHOSPHORUS AND FURNACE ACID

Furnace Charge Preparation

1. Function - This process (See Figure 8) receives low grade rock and/or phosphate rock concentrates. It produces prepared furnace charge for the electric furnace process, Process 34.

   Usually some agglomeration process is used to obtain a furnace burden with adequate porosity so that gases can escape from the furnace. Processes often used include sintering, nodulizing, or pelletizing plus calcining.

   Sintering involves mixing fine ore with coke or coal and burning on a moving grate under a strong draft. Heat from the burning coke or coal fuses the phosphatic material into a coherent mass. This material is then crushed and screened with undersized particles being returned for reprocessing.

   Nodulizing involves heating phosphate fines in a rotary kiln to incipient fusion. The tumbling in the kiln causes the material to cohere and form spheroidal agglomerates. Feed may be relatively dry or a wet slurry. Techniques for mixing the feed include using pug mixers; crane-bucket mixing; pile building, blending, and reclaiming; chaser mills; and layering on conveyor belts. Processing includes rotary drying (dry kiln), cooling of the kiln product (inclined grate cooler), crushing, and screening. Mud rings which form on kiln walls near the discharge end are removed periodically with a boring bar.

   Pelletizing plus calcining begins by blending phosphatic materials with water and binders and extruding the resulting plastic material. Pellets are formed, dried, screened, and burned in a rotary kiln just below the fusion temperature of the rock. Equipment used for this process includes pug mills, pan mills, pelletizing drums, rotary driers, screens, and rotary kilns. Two of the best binding materials are phosphoric acid and sulfuric acid.

2. Input Materials - 10 to 13 metric tons phosphatic materials per metric ton phosphorus.

3. Operating Parameters

   - Sintering
     - Moving grates - ~15 meters long.
   - Nodulizing
     - Kiln - 40 to 120 meters long x 2.5 to 4 meters diameter.
     - Kiln rotation - 1 to 3 revolutions per minute.
     - Temperature - 1200 to 1500°C.
     - Fuel - carbon monoxide from the electric furnace plus coal or oil.

- Pelletizing plus calcining
  - Pan mills - ~4 meters diameter.
  - Pelletizing drums - 12 meters long x 3.5 meters diameter with 2 cm angle lifters.
  - Kiln temperature - ~1100-1200°C.
- Preferred particle size for electric furnace - 1/2 to 5 cm in diameter.

4. Utilities

- Fuel (includes CO from the furnace which is often used as fuel) for drying and for burning - 3×10^6 to 8×10^6 kcal per metric ton elemental phosphorus.
- Electrical energy - 50 kWh per metric ton elemental phosphorus.
- Water - 0 to 2 metric tons per metric ton elemental phosphorus.

5. Waste Streams - Combustion product gases from dryers, the sintering grate, nodulizing kiln, and calcining kiln contain fluorine. The amount of fluorine emitted is approximately 0.1 to 0.2 metric tons per metric ton elemental phosphorus produced. Combustion product gases contain other pollutants in addition to fluorine.

6. EPA Classification Code - None exists.

7. References

Hurst, T. L. Chapter 18. In: Phosphorus and Its Compounds, Van Wazer, J. R. (ed.). New York, Interscience Publishers, Inc., 1961. 2:1163-1169.

Van Wazer, J. R. Phosphorus and the Phosphides. In: Kirk-Othmer Encyclopedia of Chemical Technology, 2nd Edition. Standen, A. (ed.). New York, Interscience Publishers, Inc., 1968. 15:281-282.

Electric Furnace Process

1. Function - Essentially, the process (See Figure 8) generates gaseous, elemental phosphorus by the electrothermal reduction of either phosphate rock from Process 3 or phosphate rock concentrates from Process 2, Figure 2. Coke, added to the ground rock, is the direct reducing agent. The chief product of the process is a high temperature, gaseous mixture of phosphorus and carbon monoxide, containing minor concentrations of other gaseous constituents and particulates. Ferro-phosphorus (almost always) and slag (invariably) are also produced.

   The gaseous product is forwarded to either Process 35 or 36. Ferro-phosphorus is marketed as an industry end product, and the slag is either a waste material or, if marketed, an industry by-product.

   The process is conducted inside a specially designed, continuosly operated arc furnace. The gaseous product is continuously withdrawn. The two solid products are both withdrawn intermittently from the furnace in the molten state.

   The use of this process will probably sharply decline in the near future. The recent drastic cost increase of electric power has already given an economic advantage to the wet process, the alternate source of the phosphoric acid produced as the principal downstream indirect product of the electric furnace process.

2. Input Materials - Referred to one metric ton of liquid, elemental phosphorus:

   - Phosphatic furnace charge (from Process 33) - ~10 metric tons.
   - Silica (lumps of silica rock) - 1.4 to 1.7 metric tons.
   - Coke (lumps) - 1.4 to 1.6 metric tons.
   - Iron (slugs) - ~100 to 200 kg.
   - Electrical energy (to furnace electrodes only) - 14,300 to 14,500 kWh.

3. Operating Parameters

   - Essentially atmospheric pressure.
   - Maximum furnace temperature - ~1600°C.
   - Furnaces operate with ~300 volts between electrodes, use 3-phase power.
   - Typical furnace capacity - 50,000 to 70,000 kW.
   - Approximate physical size of furnace - 17 m diameter x 17 m high, dome roof.

4. Utilities - Referred to one metric ton of liquid elemental phosphorus:

   - Motor power - ~50 to 100 kWh.
   - Cooling water (once-through basis) - 500 to 1000 m^3.

5. Waste Streams - Referred to one metric ton of liquid elemental phosphorus:

   - Fugitive atmospheric emissions (surmised only) consisting of dust-laden CO, escaping the furnace during charging operations and from electrode ports - no quantifying information available; estimated at <1m^3.
   - Slag - 8.5 to 9.5 metric tons; used as landfill if no market exists.

6. EPA Classification Code - None exists.

7. References

Faith, W. L., D. B. Keyes, and R. L. Clark. Industrial Chemical, 3rd Edition. New York, John Wiley & Sons, 1965. p. 605-606.

Shreve, R. N. Chemical Process Industries, 3rd Edition. New York, McGraw-Hill, 1967. p. 265-270.

Van Wazer, J. R. Phosphorus and the Phosphides. In: Kirk-Othmer Encyclopedia of Chemical Technology, 2nd Edition. New York, Interscience Publishers, 1968. 15:281-289.

Off-Gas Combustion

1. Function - This process (See Figure 8) burns furnace off-gas from the electric furnace process, Process 34, to form a gaseous mixture of $P_2O_5/CO_2/$and N_2 which is sent to absorption/purification, Process 39.

   Furnace off-gas is approximately 90 mol percent CO, 7 mol percent P_4, with the remainder being primarily silicon tetrafluoride and dust. The dust is removed usually by electrostatic precipitators. The clean gases are then mixed with air and the phosphorus is oxidized to P_2O_5 while the carbon monoxide is oxidized to carbon dioxide. The resulting gaseous mixture consisting primarily of P_2O_5, CO_2, and N_2 is cooled and forwarded to Process 37. Dust collected in the electrostatic precipitator is slurried with water, dried, and sold as fertilizer.

2. Input Materials

   - 800 cubic meters furnace off-gas per metric ton H_3PO_4(100% H_3PO_4).
   - 3100 to 4500 cubic meters air per metric ton H_3PO_4 (100% H_3PO_4).

3. Operating Parameters

   - Pressure - 1.5 kg/cm^2.
   - Temperature - up to 2000°C.
   - Electrostatic precipitators - two-pass with 75,000 volts between electrodes.
   - Dust collected amounts to 0.05 metric tons per metric ton elemental phosphorous produced. It contains 20 to 40% P_2O_5, 12 to 16% K_2O, 6 to 16% CaO, 18 to 30% SiO_2, 1 to 4% C, and 1 to 6% F.

4. Utilities

   - Electrical energy - 3 kWh per metric ton H_3PO_4 (100 % H_3PO_4).
   - Cooling water - 300 cubic meters per metric ton H_3PO_4 (100% H_3PO_4).

5. Waste Streams - Some of the dust collected in the electrostatic precipitator is wasted.

6. EPA Classification Code - None exists.

7. References

   Faith, W. L. D. B. Keyes, and R. L. Clark. Industrial Chemicals, 3rd Edition. New York, John Wiley & Sons, Inc., 1965. p. 599-600.

Hardesty, J. Q., and L. B. Hein. Chapter 18. In: Riegel's Handbook of Industrial Chemistry, 7th Edition. Kent, J. A. (ed.). New York, Van Nostrand Reinhold Company, 1974. p. 542.

Hurst, T. L. Chapter 18. In: Phosphorus and Its Compounds. Van Wazer, J. R. (ed.). New York, Interscience Publishers, Inc., 1961. 2:1197-1201.

Van Wazer, J. R. Phosphorus and the Phosphides. In: Kirk-Othmer Encyclopedia of Chemical Technology, 2nd Edition. Standen, A. (ed.). New York, Interscience Publishers, Inc., 1968. 15:284-286.

Phosphorus Recovery

1. Function - This process (See Figure 8) receives furnace off-gas from the electric furnace process, Process 34, and separates phosphorus in the gas from CO and N_2. The phosphorus can be sold or sent to phosphorus combustion, Process 52. The CO/N_2 gas is used as fuel or flared.

   Furnace off-gas is approximately 90 mol percent CO, 7 mol percent P_4, with the remainder being primarily silicon tetrafluoride and dust. The dust is removed usually by electrostatic precipitators and sometimes by impingement. The clean gases then enter a tower, usually flowing countercurrent to water spray. Phosphorus is condensed and runs into a sump along with any dust that was not previously removed. The liquid phosphorus is pumped into storage tanks where the last traces of dust (mud) fall to the bottom. Mud is filtered from phosphorus in some cases using porous tube filters or plate and frame-type filters. Uncondensed $CO/N_2/P_4$ gas from the spray tower is used as fuel or flared. Dust collected in the electrostatic precipitator is sprayed or slurried with water, dried, and sold as fertilizer. Phosphorus is covered with water both in the sump pit below the condenser and in storage tanks.

2. Input Materials - 2400 cubic meters furnace off-gas per metric ton elemental phosphorus.

3. Operating Parameters

   - Furnace off-gas temperature - 200 to 400°C.
   - Spray tower - 12 meters tall x 1.5 meters diameter.
   - Condensed phosphorus temperature - ~55°C.
   - Electrostatic precipitators - two-pass unit; with 48 steel tubes per unit and with a vertical steel wire in the center of each tube; 75,000 volts between wire and tube.
   - Dust collected in electrostatic precipitator amounts to approximately 0.05 metric tons per metric ton elemental phosphorus produced. It contains 20 to 40% P_2O_5, 12 to 16% K_2O, 6 to 16% CaO, 18 to 30% SiO_2, 1 to 4% C, and 1 to 6% F.

4. Utilities

   - Cooling water - 30 cubic meters per metric ton elemental phosphorus.
   - Electrical energy - 1 kWh per metric ton elemental phosphorus.

5. Waste Streams

- Solids filtered or settled from liquid phosphorus are usually returned to the electric furnace, Process 34. In some cases, filtered solids are discarded.
- Some of the dust collected in the electrostatic precipitator is wasted.

The uncondensed CO/N_2 gas is used as fuel or flared. This stream amounts to 3 metric tons per metric ton elemental phosphorus produced. It contains 0.003 to 0.03 metric tons phosphorus per metric ton phosphorus produced.

- Water used to condense phosphorus is recirculated until it becomes saturated with fluosilicates from hydrolysis of silicon tetrafluoride. It also contains small amounts of phosphorus. Additives such as soda ash or lime are made to keep it from becoming too acidic. In some cases, calcium phosphate and calcium fluosilicate which are formed by reaction of impurities in the water with additives may be removed by centrifuge or thickeners before the water is disposed of.

6. EPA Classification Code - None exists.

7. References

Hurst, T. L. Chapter 18. In: Phosphorus and Its Compounds. Van Wazer, J. R. (ed.). New York, Interscience Publishers, Inc., 1961. 2:1194-1209.

Van Wazer, J. R. Phosphorus and the Phosphides. In: Kirk-Othmer Encyclopedia of Chemical Technology, 2nd Edition. Standen, A. (ed.). New York, John Wiley & Sons, Inc., 1968. 15:285-286.

Phosphorus Combustion

1. Function - This process (See Figure 8) oxidizes phosphorus from phosphorus recovery, Process 36, to form phosphorus pentoxide (P_2O_5) plus nitrogen. This gaseous mixture is sent to absorption/purification (Process 39) or to P_2O_5 recovery, Process 38.

   Molten phosphorus is sprayed into a combustion chamber with air or air and steam. Both vertical and horizontal chambers are used. The chamber is cooled by running water down its exterior surface or it can be cooled by running phosphoric acid down the interior walls of the chamber. In the latter case, the phosphoric acid absorbs P_2O_5 as well as heat. Gas leaving the combustion chamber may be cooled in a heat exchanger before forwarding to the next process.

   If the mixture is to be forwarded to Process 38, it is necessary that the phosphorus combustion occur using dry air.

2. Input Materials

   - 0.33 metric tons phosphorus per metric ton H_3PO_4 (100% H_3PO_4).
   - 1500 to 2500 cubic meters air per metric ton H_3PO_4 (100% H_3PO_4).
   - ~0 to .05 metric tons steam per metric ton H_3PO_4 (100% H_3PO_4).

3. Operating Parameters

   - Temperature range in combustion chamber - 200 to 2000°C.
   - Combustion chamber - graphite blocks or stainless steel, 11 meters tall x 5 meters diameter.
   - Pressure - 1.5 kg/cm^2.

4. Utilities

   - Cooling water - 100 cubic meters per metric ton H_3PO_4.
   - Electrical energy - 3 kWh per metric ton H_3PO_4.

5. Waste Streams - None exists.

6. EPA Classification Code - None exists.

7. References

Hardesty, J. Q., and L. B. Hein. Chapter 18. In: Riegel's Handbook of Industrial Chemistry, 7th Edition. Kent, J. A. (ed.). New York, Van Nostrand Reinhold Company, 1974. p. 542-544.

Hurst, T. L. Chapter 18. In: Phosphorus and Its Compounds. Van Wazer, J. R. (ed.). New York, Interscience Publishers, Inc., 1961. 2:1209-1213.

Shreve, R. N. Chemical Process Industries, 3rd Edition. New York, McGraw-Hill Book Company, 1967. p. 279-281.

Van Wazer, J. R. Phosphoric Acids and Phosphates. In: Kirk-Othmer Encyclopedia of Chemical Technology, 2nd Edition. New York, John Wiley & Sons, Inc., 1968. 15:257-261.

PRODUCTION OF ELEMENTAL PHOSPHORUS AND FURNACE ACID

PROCESS NO. 38

P_2O_5 Recovery

1. Function - This process (See Figure 8) receives a dry gaseous mixture consisting primarily of P_2O_5 and N_2 from phosphorus combustion (Process 37). The P_2O_5 is separated from the other components of the gas and is sold.

   The gaseous mixture from Process 37 is cooled in a large chamber called a "barn." The chamber is cooled externally with air or water. Within this chamber, rapid mixing with cool gas causes condensation of P_2O_5.

2. Input Materials - 1700 to 3000 cubic meters P_2O_5/N_2 gas per metric ton P_2O_5.

3. Operating Parameters

   •Temperature - below 200°C.
   •Pressure - slightly above atmospheric.

4. Utilities - Cooling water - 200 metric tons per metric ton P_2O_5.

5. Waste Stream - Gases passing through the condensing chamber are emitted to the atmosphere. The gas is primarily nitrogen. It amounts to 1700 to 3000 cubic meters per metric ton P_2O_5 produced. It contains trace amounts of nitrogen oxides and P_2O_5.

6. EPA Classification Code - None exists.

7. References

Van Wazer, J. R. Phosphorus and Its Compounds. New York, Interscience Publishers, Inc., 1958. 1:268.

Van Wazer, J. R. Phosphorus Compounds. In: Kirk-Othmer Encyclopedia of Chemical Technology, 2nd Edition. New York, John Wiley & Sons, Inc., 1968. 15:313-314.

Absorption/Purification

1. Function - This process (See Figure 8) receives mixed $P_2O_5/CO_2/N_2$ gases from off-gas combustion (Process 35) or mixed P_2O_5/N_2 gases from phosphorus combustion (Process 37) and produces superphosphoric acid or furnace acid by contacting the gases with water.

   Mixed gases from Process 35 or 37 pass through an absorption tower (hydrator) countercurrent to sprayed water. Vapors from the hydrator pass to equipment which separates entrained acid mist from the CO_2/N_2 tail gas. Equipment used can include:

   - Electrostatic precipitator
   - Scrubbing tower.
   - Cyclone
   - Glass-wool filter

   The acid from the hydrator and clean-up system is combined and purified. Arsenic and lead are removed by treatment with hydrogen sulfide. The addition of finely powdered silica removes hydrofluoric acid. Excess silica, arsenic trisulfide, and other suspended solids are removed by passing the acid through a sand filter. The concentration of furnace acid produced (usually 85%) depends on the amount of water used in the hydrator and clean-up system.

   Superphosphoric acid is made by contacting the mixed gases from Process 35 or 37 with phosphoric acid in the hydrator rather than contacting them with water. Superphosphoric acid is 72 to 83% P_2O_5, corresponding to 100 to 112% H_3PO_4.

2. Input Materials

   - 1250 to 2300 cubic meters P_2O_5/N_2 gas from phosphous combustion per metric ton H_3PO_4 (100% H_3PO_4) or
   - 3500 cubic meters $P_2O_5/CO_2/N_2$ gas from off-gas combustion per metric ton H_3PO_4 (100% H_3PO_4).
   - 0.17 to 0.3 cubic meters water per metric ton H_3PO_4 (100% H_3PO_4).
   - ~0.1 cubic meters hydrogen sulfide per metric ton H_3PO_4 (100% H_3PO_4).
   - ~0.001 metric tons silica per metric ton H_3PO_4 (100% H_3PO_4).

3. Operating Parameters (for 100 metric tons of 100% H_3PO_4 per day plant)

   - Hydrator - 3 meters diameter x 11 meters tall with walls that are acid-proof, hard-burned shale and stiff-mud brick plus a 11.4 cm thick carbon brick lining.

- 18 spray nozzles to spray water into hydrator.
- Electrostatic precipitator with 100 carbon tubes, 25 cm in diameter, and 4 meters long with a stainless steel wire down the center of each tube.

4. Utilities

- Electrical energy - 5 kWh per metric ton H_3PO_4 (100% H_3PO_4).
- Cooling water - 60 cubic meters per metric ton H_3PO_4 (100% H_3PO_4).

5. Waste Streams

- Tail gases amounting to 3500 to 5000 cubic meters per metric ton H_3PO_4 produced are emitted to the atmosphere. This gas contains P_2O_5 amounting to 0.1 to 1.5 kg per metric ton H_3PO_4 (100%) produced. This gas also contains nitrogen oxides amounting to .05 kg per metric ton H_3PO_4 produced. Most of the gas is nitrogen or nitrogen plus carbon dioxide.
- Some H_2S may be emitted from the purification process. This amounts to less than 0.01 kg per metric ton H_3PO_4 produced.
- Sand from the sand filter is periodically discarded. It contains arsenic trisulfide silica, and other solids removed from the acid product.

6. EPA Classification Code - None exists.

7. References

Faith, W. L., D. B. Keyes, R. L. Clark. Industrial Chemicals, 3rd Edition. New York, John Wiley & Sons, Inc., 1965. p. 599-608.

Hardesty, J. Q., ahd L. B. Hein. Chapter 18. In: Riegel's Handbook of Industrial Chemistry, 7th Edition. Kent, J. A. (ed.). New York, Van Nostrand Reinhold Company, 1974. p. 542-544.

Heller, A. N., S. T. Cuffe, and D. R. Goodwin. Chapter 38. In: Air Pollution, 2nd Edition. Stern, A. C. (ed.). New York, Academic Press, 1968. 3:200-201.

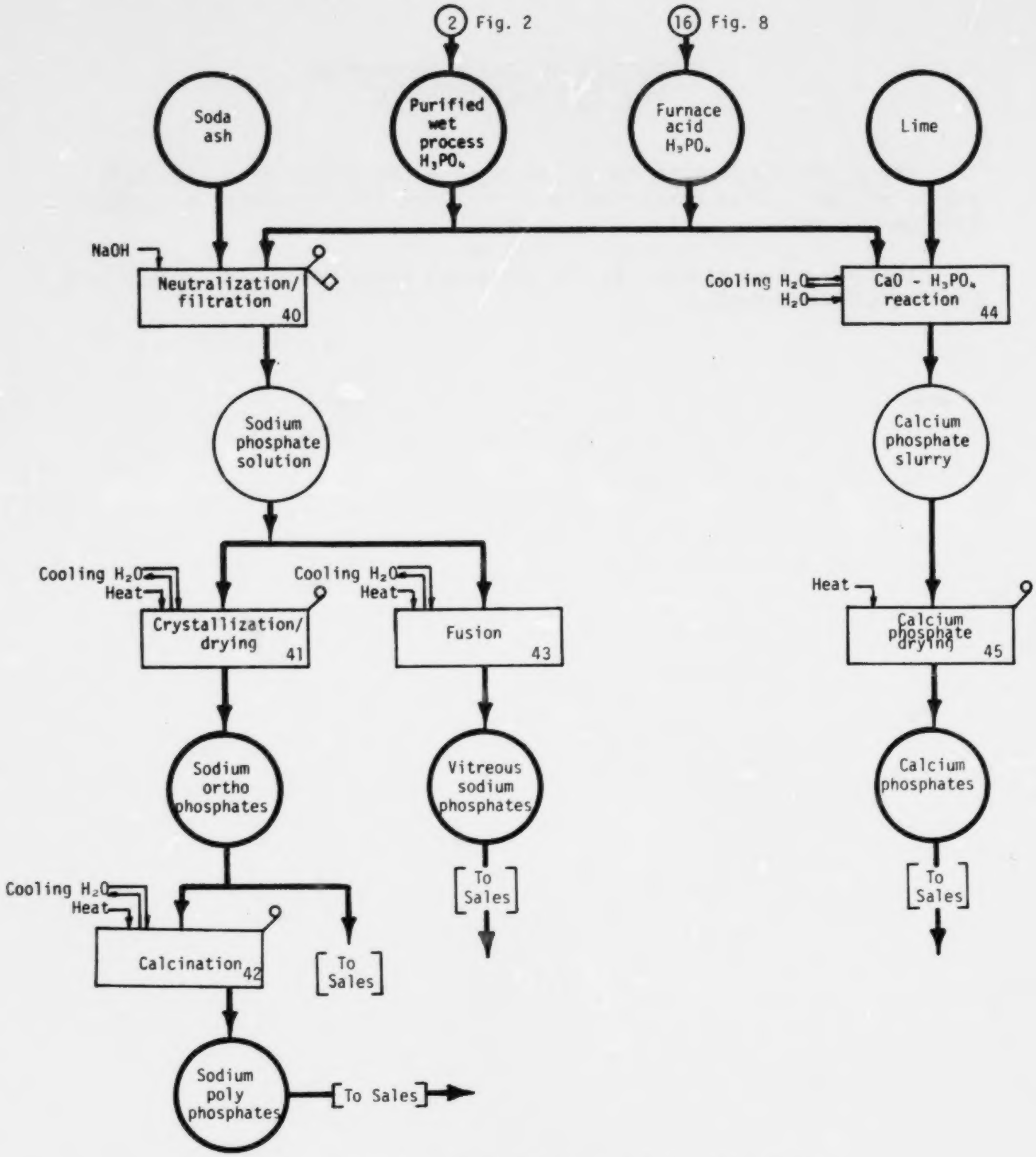
Hurst, T. L. Chapter 18. In: Phosphorus and Its Compounds. Van Wazer, J. R. (ed.). New York, Interscience Publishers, Inc., 1961. 2:1209-1213.

Van Wazer, J. R. Phosphoric Acids and Phosphates. In: Kirk-Othmer Encyclopedia of Chemical Technology, 2nd Edition. New York, John Wiley & Sons, Inc., 1968. 15:257-261.

PRODUCTION OF SODIUM PHOSPHATES AND CALCIUM PHOSPHATES

The processes in this operation combine phosphoric acid with soda ash to produce sodium phosphates and with lime (or limestone) to produce calcium phosphates.

This operation belongs to the Elemental Phosphorous and Furnace Acid Segment of the industry.



2 Fig. 2
16 Fig. 8
Soda ash
Purified wet process H_3PO_4
Furnace acid H_3PO_4
Lime
NaOH
Neutralization/ filtration 40
Cooling H_2O
H_2O
$CaO - H_3PO_4$ reaction 44
Sodium phosphate solution
Calcium phosphate slurry
Cooling H_2O
Heat
Crystallization/ drying 41
Cooling H_2O
Heat
Fusion 43
Heat
Calcium phosphate drying 45
Sodium ortho phosphates
Vitreous sodium phosphates
Calcium phosphates
To Sales
To Sales
Cooling H_2O
Heat
Calcination 42
To Sales
Sodium poly phosphates
To Sales

Figure 9. SODIUM PHOSPHATES AND CALCIUM PHOSPHATES

Neutralization/Filtration

1. Function - This process (See Figure 9) produces sodium phosphate solutions which are forwarded to crystallization/drying (Process 41) or fusion (Process 43).

   Sodium carbonate (Na_2CO_3) solution and phosphoric acid (H_3PO_4) from Figure 2 or 8 are fed to a mixing tank. A slight excess of Na_2CO_3 over the theoretical amount required to form disodium orthophosphate (Na_2HPO_4) is added and the solution is boiled with steam until all carbon dioxide is driven off. The resulting disodium phosphate solution is filtered. White mud, consisting of silica plus iron and aluminum phosphates remains on the filters. This mud is either discharged to waste or is utilized as a fertilizer material. The Na_2HPO_4 solution is processed in different ways according to the desired product.

   - Monosodium orthophosphate (NaH_2PO_4) product - The solution is diluted with H_3PO_4 to give a composition corresponding to NaH_2PO_4 and then forwarded to Process 41.
   - Na_2HPO_4 product - The solution is forwarded to Process 41.
   - Trisodium orthophosphate (Na_3PO_4) product - The solution is mixed with sodium hydroxide to give a composition corresponding to Na_3PO_4, then filtered on a rotating leaf pressure filter, and then forwarded to Process 41.
   - Vitreous sodium phosphate products - The solution composition is adjusted with a H_3PO_4 addition and forwarded to Process 43.
   - Sodium polyphosphates - The solution composition is adjusted with a H_3PO_4 addition and is forwarded to Process 41 or Process 42.

2. Input Materials (for selected products)

   - Phosphoric acid (62% basis)
     - 1.2 metric tons per metric ton $NaH_2PO_4 \cdot H_2O$ or
     - 0.45 metric tons per metric ton $Na_2HPO_4 \cdot 12H_2O$ or
     - 0.45 metric tons per metric ton $Na_3PO_4 \cdot 12H_2O$ or
     - 1.5 metric tons per metric ton $Na_2H_2P_2O_7$ (sodium-acid pyrophosphate) or
     - 1.2 metric tons per metric ton $Na_4P_2O_7$ (tetrasodium pyrophosphate) or
     - 1.3 metric tons per metric ton $Na_5P_3O_{10}$ (sodium tripolyphosphate) or
     - 1.5 metric tons per metric ton vitreous sodium phosphate.
   - Na_2CO_3 (100% basis)
     - 0.4 metric tons per metric ton $NaH_2PO_4 \cdot H_2O$ or
     - 0.3 metric tons per metric ton $Na_2HPO_4 \cdot 12H_2O$ or
     - 0.3 metric tons per metric ton $Na_3PO_4 \cdot 12H_2O$ or
     - 0.5 metric tons per metric ton $Na_2H_2P_2O_7$ or
     - 0.8 metric tons per metric ton $Na_4P_2O_7$ or
     - 0.75 metric tons per metric ton $Na_5P_3O_{10}$ or
     - 0.6 metric tons per metric ton vitreous sodium phosphate.

- Sodium hydroxide (50% basis)
  0.22 metric tons per metric ton $Na_3PO_4 \cdot 12H_2O$.

3. Operating Parameters

- Plant capacities - 30,000 to 70,000 metric tons per year.
- Temperature in mixer approximately 100°C.
- Temperature during filtration - 85 to 100°C.
- Rotating leaf pressure filter.

4. Utilities

- Electrical energy - <1 kWh per metric ton product.
- Steam - 10,000 kcal per metric ton product.

5. Waste Streams

- White mud from filtration consisting primarily of silica plus aluminum and iron phosphates may be wasted. This mud may be as high as 0.1 metric ton per metric ton of product.

- Carbon dioxide in the vapor coming from the mixing tank is released to the atmosphere. It is estimated to range from 0.12 to 0.17 metric tons per metric ton of product for the products listed under input materials.

6. EPA Classification Code - None exists.

7. References

Faith, W. L., D. B. Keyes, and R. L. Clark. Industrial Chemicals, 3rd Edition. New York. John Wiley & Sons, Inc., 1965. p. 699-706.

Van Wazer, J. R. Phosphoric Acids and Phosphates. In: Kirk-Othmer Encyclopedia of Chemical Technology, 2nd Edition. New York, John Wiley & Sons, Inc., 1968. 15:262-266.

Crystallization/Drying

1. Function - This process (See Figure 9) receives filtered sodium phosphate solutions from Process 40 and either crystallizes, or crystallizes and dries the orthosphosphate. The sodium orthophosphates can be sold or calcined in Process 42 to form sodium polyphosphates.

   Disodium orthophosphate solution is cooled in a crystallizer to yield $Na_2HPO_4 \cdot 12H_2O$. The crystals are centrifuged and packaged in moisture proof containers while the mother liquor is returned to the neutralization tank of Process 40. The crystals may be dried to yield $Na_2HPO_4 \cdot 2H_2O$ or Na_2HPO_4.

   Solution corresponding to the composition of monosodium orthophosphate is evaporated to yield crystals of $NaH_2PO_4 \cdot H_2O$. Dessicating the hydrate at ambient temperature results in the formation of NaH_2PO_4.

   Solution corresponding to the composition of trisodium orthophosphate is passed into batch-type vacuum crystallizers. Crystals of $Na_3PO_4 \cdot 12H_2O$ form and separate in a settler. Liquor is concentrated in a double-effect evaporator and returned to the neutralization tank of Process 40. Settled $Na_3PO_4 \cdot 12H_2O$ crystals are separated from remaining liquor on rotary vacuum filters, dried in rotary driers below 70°C, screened, and packaged.

   Mixed solutions of mono- and disodium orthophosphates may be spray dried before forwarding to calcination, Process 42.

2. Input Materials (selected products)

   - Mono sodium orthophosphate solution.
     2 metric tons solution per metric ton $NaH_2PO_4 \cdot H_2O$ or
     2.5 metric tons solution per metric ton $Na_2H_2P_2O_7$(sodium acid pyrophosphate).
   - Disodium orthophosphate solution.
     1.3 metric tons solution per metric ton $Na_2HPO_4 \cdot 12H_2O$ or
     3.5 metric tons solution per metric ton $Na_4P_2O_7$ (tetra sodium pyrophosphate).
   - Trisodium orthophosphate solution.
     1.5 metric tons solution per metric ton $Na_3PO_4 \cdot 12H_2O$.
   - Sodium orthophosphate solution (mixed).
     2 metric tons solution per metric ton $Na_5P_3O_{10}$ (sodium tripolyphosphate).

3. Operating Parameters - No information available.

4. Utilities

- Electrical energy - <1 kWh per metric ton product.
- Cooling water - 0 to 3 metric tons per metric ton product depending on product.
- Steam for drying and evaporation - 0 to 2 metric tons per metric ton product depending on product.
- Fuel for spray drying - 1 x 10^6 kcal per metric ton $Na_5P_3O_{10}$.

5. Waste Streams - Combustion gases may contain particulates. No quantitative data are available.

6. EPA Classification Code - None exists.

7. References

Faith, W. L., D. B. Keyes, and R. L. Clark. Industrial Chemicals, 3rd Edition. New York, John Wiley & Sons, Inc., 1965. p. 699-706.

Hurst, T. L. Chapter 18. In: Phosphorous and Its Compounds. Van Wazer, J. R. (ed.). New York, Interscience Publishers, Inc., 1961. 2:1213-1220.

Van Wazer, J. R. Phosphoric Acids and Phosphates. In: Kirk-Othmer Encyclopedia of Chemical Technology, 2nd Edition. New York, John Wiley & Sons, Inc., 1968. 15:262-266.

Calcination

1. Function - This process (See Figure 9) receives sodium phosphate solution from Process 40 or dry sodium phosphates from Process 41 and heats the input material, usually in a rotary kiln, to form a variety of sodium polyphosphate products. Grinding of products may be required before bagging or bulk shipping.

   Sodium phosphate solutions from Process 40 can be sprayed into a rotary continuous kiln where drying, molecular dehydration, conversion to polyphosphate, annealing, and cooling take place.

   Alternately dried sodium phosphates from Process 41 can be used as kiln feed.

   Annealing is necessary in both schemes to prevent products from reverting to different forms.

   Products and raw materials include but are not limited to the following:

   - Sodium acid pyrophosphate ($Na_2H_2P_2O_7$) from monosodium phosphate (NaH_2PO_4).
   - Tetrasodium pyrophosphate ($Na_4P_2O_7$) from disodium phosphate (Na_2HPO_4).
   - Sodium tripolyphosphate ($Na_5P_3O_{10}$) from mixed mono- and disodium phosphate solution.

2. Input Materials

   - 1.1 metric tons NaH_2PO_4 (anhydrous) per metric ton $Na_2H_2P_2O_7$ product.
   - 2.7 metric tons $Na_2HPO_4 \cdot 12H_2O$ per metric ton $Na_4P_2O_7$ or 3.5 metric tons disodium phosphate solution per metric ton $Na_4P_2O_7$.
   - 2 metric tons mixed mono- and disodium phosphate solution per metric ton $Na_5P_3O_{10}$.

3. Operating Parameters

   - $Na_2H_2P_2O_7$ from NaH_2PO_4.
     225 to 250°C for 6 to 12 hours.
   - $Na_4P_2O_7$ from $Na_2HPO_4 \cdot 12H_2O$.
     300 to 900°C.
   - $Na_5P_3O_{10}$ from mixed NaH_2PO_4 and Na_2HPO_4 solution.
     Solution composition - 1 mole NaH_2PO_4 to 2 moles Na_2HPO_4.

4. Utilities

   - Electrical energy - 1 to 10 kWh per metric ton product.

- Fuel - 300,000 to 2,500,000 kcal per metric ton product depending on product.
- Cooling water - up to 10 cubic meters water per metric ton product.

5. Waste Streams - Combustion gases from kilns may contain sulfur oxides and nitrogen oxides. No quantitative data are available.

6. EPA Classification Code - None exists.

7. References

Faith, W. L., D. B. Keyes, and R. L. Clark. Industrial Chemicals, 3rd Edition. New York, John Wiley & Sons, Inc., 1965. p. 699-706.

Hurst, T. L. Chapter 18. In: Phosphorous and Its Compounds. Van Wazer, J. R. (ed.). New York, Interscience Publishers, Inc., 1961. 2:1213-1220.

Van Wazer, J. R. Phosphoric Acids and Phosphates. In: Kirk-Othmer Encyclopedia of Chemical Technology, 2nd Edition. New York, John Wiley & Sons, Inc., 1968. 15:262-266.

Fusion

1. Function - This process (See Figure 9) produces vitreous phosphates from sodium phosphate solutions from Process 40.

   Sodium orthophosphate solution is fed into one end of a rectangular furnace, where moisture is driven out. A solid mass forms which melts to a viscous liquid. The liquid fills the main body of the furnace and runs out the other end of the furnace in a steady stream.

   The melt running out of the furnace is chilled on water-cooled rolls or on a water-cooled metal belt. The product may be ground. The furnace is directly heated by oil or gas flames.

2. Input Materials

   - Mixed mono-and disodium phosphate solution.
     2 metric tons solution per metric ton vitreous sodium phosphate.

3. Operating Parameters

   - 4.5 meters wide x 9 meters long x 1.5 meters high furnace with frozen layer of melt below liquid level.
   - Melt depth - 12 to 25 cm.
   - Product composition - 63 to 66 percent P_2O_5, 0.1 to 0.4 percent H_2O, remainder Na_2O.
   - Melt temperature - 700 to 1000°C.

4. Utilities

   - Fuel for heating - 2 x 10^6 kcal per metric ton vitreous phosphate.
   - Cooling water - 10 cubic meters per metric ton vitreous phosphate.
   - Electrical energy - 5 kWh per metric ton vitreous phosphate.

5. Waste Streams - Combustion gases may contain pollutants. No quantitative data are available.

6. EPA Classification Code - None exists.

7. References

Hurst, T. L. Chapter 18. In: Phosphorous and Its Compunds. Van Wazer, J. R. (ed.). New York, Interscience Publishers, Inc., 1961. 2:1213-1220.

Van Wazer, J. R. Phosphoric Acids & PHosphates. In: Kirk-Othmer Encyclopedia of Chemical Technology, 2nd Edition. New York, John Wiley & Sons, Inc., 1968. 15:262-266.

$CaO-H_3PO_4$ Reaction

1. Function - This process (See Figure 9) forms a variety of calcium phosphate slurries from lime and phosphoric acid. The slurries are forwarded to calcium phosphate drying, Process 45.

   - Monocalcium phosphate monohydrate [$CaH_4(PO_4)_2 \cdot H_2O$] is formed by mixing H_3PO_4 (75% concentration) with hydrated lime in a Stedman pan mixer. Steam, from the heat of reaction, escapes from the pasty mass.

   - Anhydrous monocalcium phosphate [$CaH_4(PO_4)_2$] is formed when quicklime is treated with H_3PO_4 in a batch mixer. Several percent aluminum phosphate or an even smaller amount of a potassium and sodium phosphate mixture is included in the mix. After heat treatment, these additives form protective coatings on the surface of the $CaH_4(PO_4)_2$ crystals.

   - Dicalcium phosphate dihydrate ($CaHPO_4 \cdot 2H_2O$) is formed by mixing a dilute lime slurry with dilute (30 to 40%) H_3PO_4 and dissipating the heat of reaction. A Stedman pan may be used.

   - Tricalcium phosphate is prepared by adding H_3PO_4 to lime slurry.

2. Input Materials

   - $CaH_4(PO_4)_2 \cdot H_2O$ product.
     H_3PO_4(75% concentration) - 1.05 metric tons per metric ton product.
     $Ca(OH)_2$ (100% basis) - 0.3 metric tons per metric ton product.
   - $CaH_4(PO_4)_2$ product.
     H_3PO_4(75% concentration) - 1.2 metric tons per metric ton product.
     CaO - 0.25 metric tons per metric ton product.
     Aluminum phosphate additive - 0 to 0.02 metric tons per metric ton product.
     Potassium - sodium phosphate additive - 0 to 0.01 metric tons per metric ton product.
   - $CaHPO_4 \cdot 2H_2O$ product
     H_3PO_4 (35% concentration) - 1.65 metric tons per metric ton product.
     $Ca(OH)_2$ (100% basis) - 0.43 metric tons per metric ton product.
   - Tricalcium phosphate product.
     H_3PO_4 (75% concentration) - 0.8 metric tons per metric ton product.
     $Ca(OH)_2$ (100% basis) - 0.7 metric tons per metric ton product.

3. Operating Parameters

   - $CaH_4(PO_4)_2 \cdot H_2O$ product.
     Temperature in mixer ~120°C.

- $CaH_4(PO_4)_2$ product.
  Temperature in mixer ~140°C.
- $CaHPO_4 \cdot 2H_2O$
  Temperature ~25°C.
- Tricalcium phosphate.
  $CaO:P_2O_5$ mole ratio is ~3:1.

4. Utilities

- Electrical energy - <1 kWh per metric ton calcium phosphate product.
- Cooling water - 0 to 20 cubic meters per metric ton calcium phosphate product.

5. Waste Streams - None exists.

6. EPA Classification Code - None exists.

7. References

Hurst, T. L. Chapter 18. In: Phosphorous and Its Compounds. Van Wazer, J. R. (ed.). New York, Interscience Publishers, Inc., 1961. 2:1213-1220.

Van Wazer, J. R. Phosphoric Acids and Phosphates. In: Kirk-Othmer Encyclopedia of Chemical Technology, 2nd Edition. New York, John Wiley & Sons, Inc., 1968. 15:262-266.

Calcium Phosphate Drying

1. Function - This process (See Figure 9) dries various calcium phosphate slurries from Process 44. The dry products are ground and bagged or shipped in bulk.

   - Monocalcium phosphate monohydrate [$CaH_4(PO_4)_2 \cdot H_2O$] thick slurry is usually dried in a vacuum dryer.
   - Anhydrous monocalcium phosphate [$CaH_4(PO_4)_2$] is heat treated to change the protective coatings (formed by aluminum phosphate or potassium plus sodium phosphate) from orthophosphates to polyphosphates.
   - Dicalcium phosphate dihydrate ($CaHPO_4 \cdot 2H_2O$) must be dried in a tube dryer or kiln mill if powdered limestone is the source of calcium in the compound. If quicklime is used as the calcium source, no drying is necessary.
   - Tricalcium phosphate slurry is filtered and dried.

2. Input Materials

   - 1.2 metric tons $CaH_4(PO_4)_2 \cdot H_2O$ slurry per metric ton $CaH_4(PO_4)_2 \cdot H_2O$ product.
   - 1 metric ton $CaH_4(PO_4)_2$ per metric ton $CaH_4(PO_4)_2$ product.
   - 1 metric ton $CaHPO_4 \cdot 2H_2O$ per metric ton $CaHPO_4 \cdot 2H_2O$ product if quicklime is the calcium source.
   - 1.2 metric tons tricalcium phosphate slurry per metric ton tricalcium phosphate product.

3. Operating Parameters - No data available.

4. Utilities

   - Electrical energy - 5 kWh per metric ton product.
   - Fuel for heat - 0 to 200,000 kcal per metric ton product.

5. Waste Streams - Combustion gases may contain pollutants. No quantitative information is available.

6. EPA Classification Code - None exists.

7. References

Hurst, T. L. Chapter 18. In: Phosphorous and Its Compounds. Van Wazer, J. R. (ed.). New York, Interscience Publishers, Inc., 1961. 2:1213-1220.

Van Wazer, J. R. Phosphoric Acids and Phosphates. In: Kirk-Othmer Encyclopedia of Chemical Technology, 2nd Edition. New York, John Wiley & Sons, Inc., 1968. 15:262-266.

APPENDIX A

RAW MATERIALS

Raw Material List - Composition and Occurrence Information

1. Air

- Air contains 0 to 4% water vapor depending on temperature and humidity. Concentrations in ppm of the ten most prevalent elements or compounds in dry air are as follows:

N_2 - 781,000
O_2 - 209,000
Ar - 9,300
CO_2 - 330
Ne - 18
He - 5
CH_4 - 1.5
Kr - 1.1
H_2 - 0.5
N_2O - 0.5

- Air is used as a source of nitrogen in most ammonia plants.

2. Ammonium compounds (by-products from steel industry)

Ammonium sulfate
Ammonia liquor
  Grade A, 29.4% NH_3
  Grade B, 25% NH_3
  Grade C, 15 to 25% NH_3
Di- and monoammonium phosphate

3. Coke-Oven Gas

- A typical composition in mol percent of coke-oven gas which has been stripped of nitrogen, light oils, and naphthalene is as follows:

H_2 - 57%
CH_4 - 29%
Other - 4%

- Coke-oven gas provides H_2 for some ammonia plants.

4. Electrolytic Hydrogen (from chlorine cells)

- Concentrations are in mol percent.

H_2 - 92%
H_2O - 8%
Others - <0.05%

- Electrolytic H_2 is the H_2 source in some ammonia plants.

5. Iron

- Scrap iron of varying composition.
- Iron is used in making ferrophosphorus, a co-product in electric furnace phosphorus plants.

6. Lime

High-calcium lime (90 weight percent calcium oxide).
Lime is the source of calcium in calcium phosphate plants.

7. Naphtha

- Typically $CH_{2.1}$ to $CH_{2.2}$ with a molecular weight of 135 to 156.
- Naphtha is the source of H_2 for some ammonia plants.

8. Natural Gas

- Concentration ranges in mol percent for most natural gases are as follows:

0.4 to 3 N_2
86 to 95 CH_4
3 to 8 C_2H_6
0.6 to 3 C_3H_8
0 to 1 CO_2
Others total below 1%

- Natural gas is the source of H_2 for most ammonia plants.

9. Potassium Chloride

- Weight percent K_2O - 60 to 62.5.
- Bulk density (metric tons/m^3) - 0.93 to 1.3.
- Potassium chloride is used in mixed fertilizers and in making potassium nitrate.

10. Potassium Sulfate

- Weight percent K_2O - 54
- Bulk density (metric tons/m^3) - 0.94 to 1.65.
- Potassium sulfate is used in mixed fertilizers.

11. Phosphate Rock Deposits

- Representative ranges of components in commercial phosphate rocks in weight percent are as follows:

- Phosphate rock is the source of phosphorus for the fertilizer industry.

12. Refinery Off-Gas

- Concentration ranges in mol percent of components in refinery off-gas are typically as follows:

H_2 - 75 to 95
CH_4 - 1 to 10
C_2H_6 - 1 to 6
C_3H_8 - 1 to 5
C_4's - 0.4 to 2
C_5's - 0.2 to 0.8
Others total - below 1

- Refinery off-gas can be used as the source of H_2 in ammonia plants.

13. Soda Ash

- Commercial grade 99 weight percent Na_2CO_3 is used.
- Soda ash is the source of sodium in sodium phosphate and sodium polyphosphate plants.

14. Sulfur

- Sulfur from the Frasch process is the usual raw material for making sulfuric acid. Sulfur purity is usually 99.0 to 99.9 weight percent pure. Oil or cabonaceous material is typically 0.15% or less. Ash is typically 0.1% or less. H_2SO_4 is typically 0.05%.
- Sulfur is used to make sulfuric acid, principally for producing normal superphosphate and wet-process phosphoric acid.

15. Sulfuric Acid

- The usual concentration is 93 to 98 weight percent.
- Sulfuric acid is used to make normal superphosphate and wet-process phosphoric acid.
- By-product acid seldom is used because of the possible adverse effects of impurities on the phosphoric acid process.

TABLE A-1. REPRESENTATIVE ANALYSES OF COMMERCIAL PHOSPHATE ROCKS.

Location and type	P_2O_5	CaO	MgO	Al_2O_3	Fe_2O_3	SiO_2	SO_2	F	Cl	CO_2	Organic carbon	Na_2O	K_2O	H_2O*
United States														
Florida														
Land pebble, high grade	35.5	48.8	0.04	0.9	0.7	6.4	2.4	4.0	0.01	1.7	0.3	0.07	0.09	1.8
Land pebble, furnace grade	30.5	46.0	0.4	1.5	1.9	8.7	2.6	3.7	0.01	4.0	0.5	0.1	0.1	2.0
Hard rock, high grade	35.3	50.2	0.03	1.2	0.9	4.3	0.1	3.8	0.005	2.8	0.3	0.4	0.3	2.0
Hard rock, waste pond	23.0	28.5	0.4	14.8	2.9	19.8	0.01	2.1	0.005	1.4	0.3	0.1	0.4	7.0
Tennessee														
Brown rock, high grade	34.4	49.2	0.02	1.2	2.5	5.9	0.7	3.8	0.01	2.0	0.2	0.2	0.3	1.4
Brown rock, furnace grade	21.2	29.1	0.6	10.0	6.2	25.6	0.4	2.2		1.2	0.3	0.3	0.4	2.5
Western States														
Phosphoria rock, high grade	32.2	46.0	0.2	1.0	0.8	7.5	1.7	3.4	0.02	2.1	1.8	0.5	0.4	2.5
Phosphoria rock, low grade	19.0	23.3	1.4	5.9	4.0	27.4	1.9	1.8		4.0	5.0	1.5	1.0	3.5

---

* Dried at 100°C for several hours.

APPENDIX B

PRODUCT LIST

Preceding page blank

Product List - Products

Ammonia
  Anhydrous - NH_3
  Aqua - NH_3 - water solution

Ammonium nitrate - NH_4NO_3

Ammonium phosphates
  Diammonium - $(NH_4)_2HPO_4$
  Monoammonium - $(NH_4)H_2PO_4$

Ammonium phosphate nitrate - contains higher N to P ratio than diammonium phosphate.

Ammonium phosphate sulfate - contains higher N to P ratio than diammonium phosphate.

Ammonium sulfate - $(NH_4)_2SO_4$

Bulk-blended mixed fertilizers - contain N, P, and K.

Calcium phosphates
  Dicalcium - $CaHPO_4 \cdot 2H_2O$ or $CaHPO_4$
  Monocalcium - $CaH_4(PO_4)_2 \cdot H_2O$ or $CaH_4(PO_4)_2$
  Tricalcium - Mol ratio of CaO to P_2O_5 ~3 to 1.

*Chlorine (liquid) - Cl_2

Defluorinated phosphate rock - usually contains ~30 weight percent P_2O_5, <0.2 weight percent F.

Ferrophosphorus - typically 25 weight percent P, 60 to 70 weight percent Fe, others 5 to 15 weight percent.

*Fluorosilicic acid - H_2SiF_6, crude 20 to 25 weight percent aqueous solution.

Granular mixed fertilizers - contain N, P, and K

*Gypsum - $CaSO_4 \cdot 2H_2O$

Liquid mixed fertilizers - contain N, P, and K

---

* Industry by-products.

Liquid suspension - contain N, P, and K

Marketable phosphate rock - average of 31.4 weight percent P_2O_5
  Concentrates
  High-grade crushed
  Land pebble

Nitric acid - usually 52 to 67 weight percent HNO_3

Nitric phosphate - contains N, P, and K

Phosphoric acids
  Ortho
    Furnace process - usually 75 to 85 weight percent H_3PO_4
    Wet process - usually 75 to 85 weight percent H_3PO_4
  Super - usually 75 weight percent P_2O_5 which corresponds to 105 weight percent H_3PO_4

Phosphorus (liquid white) - P_4

Phosphorus pentoxide - P_2O_5

Potassium nitrate - typically 95 weight percent KNO_3

*Slag - ~40 weight percent SiO_2, ~50 weight percent CaO, ~10 weight percent other oxides.

Sodium orthophosphates
  Ortho disodium - Na_2HPO_4
  Ortho monosodium - NaH_2PO_4
  Ortho trisodium - Na_3PO_4
  Viteous sodium - 63-66 weight percent P_2O_5; 34-37 weight percent Na_2O.

Sodium poly (pyro) phosphates
  Sodium acid pyro - $Na_2H_2P_2O_7$
  Tetra sodium pyro - $Na_4P_2O_7$
  Sodium tripoly - $Na_5P_3O_{10}$

Sulfuric acid - usually 93 to 98 weight percent H_2SO_4

Superphosphates
  Normal - ~30 weight percent $CaH_4(PO_4)_2$; 10% $CaHPO_4$; 45% $CaSO_4$; 15% other or 18-20 weight percent P_2O_5
  Triple - 46 weight percent P_2O_5

Urea - NH_2CONH_2

APPENDIX C*

COMPANY/PRODUCT LISTS

---

* Companies producing each of the products shown in Appendix B, either for sale or captive use, are listed under the product name. Various forms of the same products are listed under the generic product name in cases where information sources make no distinction between the product forms produced.

TABLE C-1. PRODUCERS OF AMMONIA (ANHYDROUS AND AQUA) - NH_3

Company name	Location of operation (city and state)	Annual capacity (10^3 metric tons)	Remarks
Air Products & Chems., Inc.	New Orleans, LA	191	
	Pensacola, FL	68	
Allied Chem. Corp.			
Specialty Chems. Div.	Hopewell, VA	310	
	South Point, OH	310	
Union Texas Petroleum Div.			
Agricultural Dept.	Geismar, LA	310	
	Omaha, NB	191	
American Cyanamid Co.			
Agricultural Div.	New Orleans, LA	310	
Apache Powder Co.	Benson, AZ	14	
Beker Indust. Corp.			
Agricultural Products Corp. subsid.	Conda, ID	91	
Borden Inc.			
Borden Chem. Div.			
Petrochems. Div.	Geismar, LA	260	By-product H_2 & natural gas
CF Indust., Inc.			
Chattanooga Nitrogen Complex	Tyner, TN	150	
Donaldsonville Nitrogen Complex	Donaldsonville, LA	655	
Fremont Nitrogen Complex	Fremont, NB	45	
North Carolina Nitrogen Complex	Tunis, NC	191	
Terre Haute Nitrogen Complex	Terre Haute, IN	123	
Coastal States Gas Corp.			
Colorado Interstate Corp., subsid.			
Wycon Chem. Co., subsid	Cheyenne, WY	132	
Columbia Nitrogen Corp.	Augusta, GA	118	
Cominco American Inc.			
Camex, Inc., subsid.	Borger, TX	365	

TABLE C-1 (Continued) PRODUCERS OF AMMONIA (ANHYDROUS AND AQUA) - NH_3

Company name	Location of operation (city and state)	Annual capacity (10^3 metric tons)	Remarks
Commercial Solvents Corp.	Sterlington, LA	310	
Copperative Farm Chems. Association	Lawrence, KS	310	
Diamond Shamrock Corp.			
Diamond Shamrock Oil & Gas Co.	Dumas, TX	145	
Dow Chem. U.S.A.	Freeport, TX	105	Chlorine cells
E. I. du Pont de Nemours & Co., Inc.			
Biochems. Dept.	Belle, WV	310	
Elastomer Chems. Dept.	Baumont, TX	310	
Plastics Dept.	Victoria, TX	91	
El Paso Natural Gas Co.			
El Paso Products Co., subsid.	Odessa, TX	105	
Farmland Indust., Inc.	Dodge City, KS	191	
	Enid, OK	365	
	Fort Dodge, IA	173	
	Hastings, NB	127	
Felmont Oil Corp.	Olean, NY	77	
First Mississippi Corp.			
FIRST MISS INC., subsid	Fort Madison, IA	310	
FMC Corp.			
Chem. Group			
Indust. Chem. Div.	South Charleston, WV	23	Chlorine cells
Gardinier, Inc.			
U. S. Phosphoric Products	Tampa, FL	118	
Goodpasture, Inc.	Dimmitt, TX	77	
W. R. Grace & Co.			
Agricultural Chems. Group	Big Spring, TX	114	
	Memphis, TN	300	
Green Valley Chem. Corp.	Creston, IA	32	
Gulf + Western Indust., Inc.			
The New Jersey Zinc Co., subsid.	Palmerton, PA	36	
Hercules Inc.			
Synthetics Dept.	Hercules, CA	64	
	Louisiana, MO	64	

TABLE C-1 (Continued) PRODUCERS OF AMMONIA (ANHYDROUS AND AQUA) - NH_3

Company name	Location of operation (city and state)	Annual capacity (10^3 metric tons)	Remarks
Kaiser Aluminum & Chem. Corp.			
Kaiser Agricultural Chems. Div.	Savannah, GA	137	
Lone Star Gas Co.			
Nipak, Inc., subsid.	Kerens, TX	114	
	Pryor, OK	95	
Mississippi Chem. Corp.	Pascagoula, MS	159	
	Yazoo City, MS	360	
Mobil Oil Corp.			
Mobil Chem. Co., Div.			
Petrochems. Div.	Beaumont, TX	236	
Monsanto Co.			
Monsanto Agricultural Products Co.	Luling, LA	380	
N-Ren Corp.			
Cherokee Nitrogen Div.	Pryor, OK	50	
High Plains Div.	Plainview, TX	23	
Occidental Petroleum Corp.			
Hooker Chem. Corp., subsid.			
Hooker Chems. and Plastic Corp. subsid.			
Electrochemical & Specialty Chems. Div.	Tacoma, WA	23	Chlorine cells
Occidental Chem. Co., subsid.			
Southern Region	Plainview, TX	50	
Western Div.	Hanford, CA	23	Leased from Pennzoil Company
	Lathrop, CA	86	47% of the ammonia plant is owned by California Ammonia Company.
Olin Corp.			
Agricultural Chems. Div.	Lake Charles, LA	440	
Pennwalt Corp.			
Chem. Div.	Portland, OR	9	Chlorine cells
Phillips Pacific Chem. Co.	Kennewick, WA	141	

TABLE C-1 (Continued) PRODUCERS OF AMMONIA (ANHYDROUS AND AQUA) - NH_3

Company name	Location of operation (city and state)	Annual capacity (10^3 metric tons)	Remarks
Phillips Petroleum Co.			
Fertilizer Div.	Beatrice, NB	191	
Plastics Div.	Pasadena, TX	209	
PPG Indust., Inc.			
Chem. Div.			
Indust. Chem. Div	Natrium, WV	45	Chlorine cells & natural gas
Reichold Chems., Inc.	St. Helens, OR	82	
Rohm and Haas Co.			
Rohm and Haas Texas Inc., subsid	Deer Park, TX	45	
St. Paul Ammonia Products, Inc.	East Dubuque, IL	191	
J. R. Simplot Co.			
Minerals and Chem. Div.	Pocatello, ID	100	
Skelly Oil Co.			
Hawkeye Chem., Co., subsid.	Clinton, IA	127	
Standard Oil Co. of California	El Segundo, CA	18	Refinery waste water
	Richmond, CA	123	Natural gas and refinery wast water
Chevron Chem. Co., subsid.			
Ortho Div.	Fort Madison, IA	95	
Standard Oil Co. (Kentucky), subsid.	Pascagoula, MS	455	
Standard Oil Co. (Indiana)			
Amoco Oil Co., subsid.	Texas City, TX	635	
The Standard Oil Co. (OHio			
Vistron Corp., subsid.			
Chems. Dept.	Lima, OH	455	
Tenneco Inc.			
Tenneco Chems., Inc.			
Organics and Polymers Div.	Houston, TX	191	
Tennessee Valley Authority	Muscle Shoals, AL	59	
Terra Chems. Internat'l. Inc.	Port Neal, OA	191	
Tipperary Corp.	Lovington, NM	32	
Triad Chem.	Donaldsonville, LA	335	

TABLE C-1 (Continued) PRODUCERS OF AMMONIA (ANHYDROUS AND AQUA) - NH_3

Company name	Location of operation (city and state)	Annual capacity (10^3 metric tons)	Remarks
Tyler Corp. Atlas Powder Co., subsid.	Joplin, MO	123	
Union Oil Co. of California Collier Carbon and Chem. Corp., subsid.	Brea, Calif	245	
	Kenai, AK	473	
United States Steel Corp. USS Agri-Chemicals, Div.	Cherokee, AL	159	
	Clairton, PA	296	Coke-oven gas
	Geneva, UT	64	Coke-oven gas
Valley Nitrogen Producers, Inc.	El Centro, CA	191	
	Helm, CA	159	
Arizona Agrochemical Co., subsid.	Chandler, AZ	32	
Vulcan Materials Co. Chems. Div.	Wichita, Kans.	23	Chlorine cells
The Williams Companies Agrico Chem. Co., subsid.	Blytheville, AR	310	
	Donaldsonville, LA	310	
	Total	15,900	

TABLE C-2. PRODUCERS OF AMMONIUM NITRATE - NH_4NO_3

Company name	Location of operation (city and state)	Annual capacity (10^3 metric tons)	Remarks
Agway, Inc.	Olean, NY	68	
Air Products and Chems., Inc.	Pensacola, FL	182	
Allied Chem. Corp.			
Union Texas Petroleum Div.			
Agricultural Dept.	Geismar, LA	227	
	Omaha, NB	105	
American Cyanamid Co.			
Agricultural Div.	Hannibal, MO	123	
Apache Powder Co.	Benson, AR	59	
CF Indust., Inc.			
Chattanooga Nitrogen Complex	Tyner, TN	186	
Fremont Nitrogen Complex	Fremont, NB	36	
North Carolina Nitrogen Complex	Tunis, NC	186	
Terre Haute Nitrogen Complex	Terre Haute, IN	141	
Coastal States Gas Corp.			
Colorado Interstate Corp., subsid			
Wycon Chem. Co., subsid.	Cheyenne, WY	73	
Columbia Nitrogen Corp.	Augusta, GA	191	
	Moultrie, GA	45	
Cominco American Inc.	Beatrice, NB	154	
Commercial Solvents Corp.	Sterlington, LA	173	
Cooperative Farm Chems. Association	Lawrence, KS	245	
E. I. du Pont de Nemours & Co., Inc.			
Indust. Chems. Dept.	Gibbstown, NJ	45	
Polymer Intermediates Dept.	Du Pont, WA	18	
	Martinsburg, WV	n.a.	
	Seneca, IL	182	
Gardinier Big River, Inc.	Helena, AR	95	
Goodpasture, Inc.	Dimmitt, TX	n.a.	
W. R. Grace & Co.			
Agricultural Chems. Group	Wilmington, NC	186	

TABLE C-2 (Continued) PRODUCERS OF AMMONIUM NITRATE - NH_4NO_3

Company name	Location of operation (city and state)	Annual capacity (10^3 metric tons	Remarks
Gulf Oil Corp.			
Gulf Oil Chems. Co., Div.			
Indust. and Specialty Chems. Div.	Pittsburg, KS	314	
Hercules Inc.			
Indust. Systems Dept.	Bessemer, AL	23	
	Carthage, MO	n.a.	
	Donora, PA	136	
Synthetics Dept.	Hercules, CA	73	
	Louisiana, MO	460	
Illinois Nitrogen Co.	Marselles, IL	136	
Kaiser Aluminum & Chem. Corp.			
Kaiser Agricultural Chems. Div.	Bambridge, GA	55	
	North Bend, OH	95	
	Savannah, GA	186	
	Tempa, FL	50	
Lone Star Gas Co.			
Nipak, Inc., subsid.	Kerens, TX	50	
Mississippi Chem. Corp.	Yazoo City, Miss.	455	
Mobil Oil Corp.			
Mobil Chem. Co., Div.			
Petrochems. Div.	Beaumont, TX	177	
Monsanto Co.			
Monsanto Agricultural Products Co.	El Dorado, AL	323	
	Luling, LA	255	
Nitram, Inc.	Tampa, FL	136	
N-Ren Corp.			
Cherokee Nitrogen Div.	Pryor, OK	77	
Phillips Pacific Chem. Co.	Kennewick, WA	50	
Phillips Petroleum Co.			
Fertilizer Div.	Beatrice, NB	64	
	Etter, TX	168	

TABLE C-2 (Continued) PRODUCERS OF AMMONIUM NITRATE - NH_4NO_3

Company name	Location of operation (city and state)	Annual capacity (10^3 metric tons	Remarks
Reichold Chems., Inc.	St. Helen, OR	23	
St. Paul Ammonia Products, Inc.	Pine Bend, MN	136	
J. R. Simplot Co. Minerals and Chem. Div.	Pocatello, ID	n.a.	
Skelly Oil Co. Hawkeye Chem. Co., subsid.	Cannon, IA	136	
Standard Oil Co. of California Chevron Chem. Co., subsid. Ortho Div.	Fort Madison, IA	77	
	Kennewick, WA	77	
	Richmond, CA	41	
The Standard Oil Co. (Ohio) Viston Corp., subsid. Chems. Dept	Lima, OH	73	Leased from Solar Nitrogen
Terra Chems. Internat'l. Inc.	Port Neal, IA	136	
Tyler Corp. Atlas Powder Co., subsid.	Joplin, MO	214	Part leased from Solar Nitrogen
	Tamaqua, PA	41	
Union Oil Co. of California Collier Carbon and Chem. Corp., subsid.	Brea, CA	55	
United States Steel Corp. USS Agri-Chemicals, Div.	Cherokee, AL	91	
	Crystal City, MO	91	
	Geneva, UT	91	
Valley Nitrogen Producers, Inc.	El Centro, CA	41	
Vicksburg Chem. Co.	Vicksburg, MS	27	
The Williams Companies Agrico Chem. Co., subsid.	Henderson, KY	91	
	Total	7,440	

TABLE C-3. PRODUCERS OF AMMONIUM PHOSPHATES - $(NH_4)_2HPO_2$; $(NH_4)H_2PO_4$; NITRATE; SULFATE

Company name	Location of operation (city and state)	Annual capacity (10^3 metric tons	Remarks
American Plant Food Corp.	Galena Park, TX	159	Mostly mixtures
Beker Indust. Corp.			
Agricultural Products Corp., subsid.	Conda, ID	245	DAP
National Phosphate Corp., subsid.	Hahnville, LA	423	DAP
	Marseilles, IL	182	
Borden Inc.			
Borden Chem. Div.			
Smith-Douglass	Piney Point, FL	118	
	Streator, IL	82	Mostly mixtures
Brewster Phosphates	Geismar, LA	136	Leased from Allied Chem. Corp.
	Luling, LA	350	
CF Indust., Inc.			
Bartow Phosphate Complex	Bartow, FL	910	DAP
Plant City Phosphate Complex	Plant City, FL	355	
Engelhard Minerals & Chems. Corp.			
Conserv. Inc., subsid.			
Conserv. Chems. Div.	Nichols, FL	182	MAP
Farmland Indust., Inc.	Green Bay, FL	355	DAP
Farmers Chem. Co., subsid.	Joplin, Mo	223	Mixtures
First Mississippi Corp.			
FIRST MISS INC., subsid.	Fort Madison, IA	450	DAP and mixtures
Ford Motor Co.			
Steel Div.	Dearborn, MI	23	Coke oven by-product
Gardinier, Inc.			
U. S. Phosphoric Products	Tampa, FL	477	DAP and MAP
Gardinier Big River, Inc.	Helena, AR	136	DAP and mixtures
W. R. Grace & Co.			
Agricultural Chems. Group	Bartow, FL	391	DAP and MAP. Includes 195,000 tons/yr. that is interchangeable with TSP.

TABLE C-3 (Continued) PRODUCERS OF AMMONIUM PHOSPHATES - $(NH_4)_2HPO_4$; $(NH_4)H_2PO_4$; NITRATE; SULFATE

Company name	Location of operation (city and state)	Annual capacity (10^3 metric tons	Remarks
Heico, Inc.	Delaware Water Gap, PA		
Internat'l Minerals & Chem. Corp.			
Agricultural Operations	Bonnie, FL	45	Has produced up to 50,000 tons/yr. of feed grade DAP & MAP in a 400,000 ton/yr. feed material plant.
Kaiser Steel Corp.	Fontana, CA	23	Coke oven by-product
Lone Star Gas Co.			
Nipak, Inc., subsid.	Kerens, TX	100	Mostly mixtures
Mississippi Chem. Corp.	Pascagoula, MS	573	Mostly mixtures
Mobil Oil Corp.			
Mobil Chem. Co., Div.			
Phosphorus Div.	Depue, IL	218	DAP
Monsanto Co.			
Monsanto Indust. Chems. Co.	Trenton, MI	36	
North Idaho Phosphate Co.	Kellogg, ID	59	DAP, MAP, 16-20-0
Occidental Petroleum Corp.			
Hooker Chem. Corp., subsid.			
Occidental Chem. Co., subsid.			
Southern Region	Plainview, TX	23	
Occidental of Florida Div.	White Springs, FL	523	DAP; interchanges with TSP
Western Div.	Lathrop, CA	150	Mostly mixtures
Olin Corp.			
Agricultural Chems. Div.	Pasadena, TX	727	
Pennzoil Co.			
Pennzoil Chem., Inc., subsid.	Hanford, CA	32	MAP; possibly on a temporary basis
Royster Co.	Mulberry, FL	245	DAP
J. R. Simplot Co.			
Minerals and Chem. Div.	Pocatello, ID	218	DAP, MAP, 16-20-0

TABLE C-3 (Continued) PRODUCERS OF AMMONIUM PHOSPHATES - $(NH_4)_2HPO_4$; $(NH_4)H_2PO_4$; NITRATE; SULFATE

Company name	Location of operation (city and state)	Annual capacity (10^3 metric tons	Remarks
Standard Oil Co. of California			
Chevron Chem. Co., subsid. Ortho Div.	Fort Madison, IA	182	Ammonium phosphate nitrates
	Kennewick, WA	68	Ammonium phosphate nitrates
	Richmond, CA	91	Ammonium phosphate nitrates
Stauffer Chem. Co. Fertilizer and Mining Div.	Pasadena, TX	118	Mostly DAP and MAP
	Salt Lake City, UT	59	Mostly DAP and MAP
Tennessee Valley Authority	Muscle Shoals, AL	59	Solid ammonium polyphosphates
Texasgulf Inc. Agricultural Div.	Aurora, NC	200	DAP
Union Oil Co. of California Collier Carbon and Chem. Corp., subsid.	Nichols, CA	50	Mostly mixtures
United States Steel Corp. USS Agri-Chemicals, Div.	Cherokee, AL	223	DAP: other grades; mixtures
Valley Nitrogen Producers, Inc.	Helm, CA	127	
Agriform of Imperial Valley, subsid.	Imperial, CA	n.a.	
Arizona Agrochemical Co., subsid.	Chandler, AZ	55	
The Williams Companies Agrico Chem. Co., subsid.	Donaldsonville, LA	1,400	DAP
	Total	10,800	

DAP = diammonium phosphate, MAP = monoammonium phosphate.

NOTE: Data are shown for primary producing plants manufacturing solid nitrogen-phosphate fertilizers (with varying ratios of N to P_2O_5) based singly or jointly on (a) the ammoniation of phosphoric acid, & (b) the ammoniation of phosphoric acid plus nitric acid and/or sulfuric acid. The most important product of this type is fertilizer grade diammonium phosphate (18-46-0), made by ammoniating phosphoric acid. Many of these plants also manufacture several grades of N-P-K mixed fertilizers as indicated in the "Remarks" column. Excluded from this list are other plants that specialize in the production of N-P-K mixtures by various processes, & the many small to large liquid ammonium phosphate plants in the U. S.

TABLE C-4. PRODUCERS OF AMMONIUM SULFATE - $(NH_4)_2SO_4$

Company name	Location of operation (city and state)	Annual capacity (10^3 metric tons)	Remarks
Delta Chems., Inc.	Searsport, ME	19	
Occidental Petroleum Corp.			
Hooker Chem. Corp., subsid.			
Occidental Chem. Co., subsid.			
Southern Region	Houston, TX	127	Prime product
	Plainview, TX	91	Prime product
Western Div.	Lathrop, CA	73	Prime product
Olin Corp.			
Agricultural Chems. Div.	Pasadena, TX	11	Prime product
Indust. Products & Services Div.	Beaumont, TX	11	Prime product
Quality Chems. Ltd.	Baltimore, MD	5	
J. R. Simplot Co.			
Minerals and Chem. Div.	Pocatello, ID	32	
Standard Oil Co. of California			
Chevron Chem. Co., subsid.			
Ortho Div.	Richmond, CA	82	May Close
Valley Nitrogen Producers, Inc.	Helm, CA	264	
	Total	715	

TABLE C-5. PRODUCERS OF BULK-BLENDED MIXED FERTILIZERS - CONTAIN N, P, AND K

See Directory at the end of this section.

TABLE C-6. PRODUCERS OF CALCIUM PHOSPHATES

Company name	Location of operation (city and state)	Annual capacity (10^3 metric tons)	Remarks
Calcium phosphate			
Dicalcium phosphate - $CaHPO_4 \cdot 2H_2O$ or $CaHPO_4$			
American Cyanamid Co.			
Agricultural Div.	Alden, Ia Hannibal, Mo Weeping Water, NB		
Eastman Kodak Co.			
Eastman Gelatine Corp.	Peabody, MA		
Farmland Indust. Inc.			
Farmers Chem. Co., subsid.	Joplin, MO		
Internat'l Minerals & Chem. Corp.			
Agricultural Operations	Bonnie, FL		
Mallinokrodt, Inc.			
Indust. Chems. Div.	St. Louis, Mo		
Edward Mendell Co., Inc.			
Chems. Div.	Carmel, NY		
Monsanto Co.			
Monsanto Indust. Chems. Co.	Carondelet, MO		
Occidental Petroleum Corp.			
Hooker Chem. Corp. subsid.			
Occidental of Florida Div.	Davenport, IA		
Richardson-Merrell, Inc.			
J. T. Baker Chem. Co., subsid.	Phillipsburg, NJ		
Stauffer Chem. Co.			
Indust. Chem. Div.	Chicago Heights, IL Nashville, TN		
Monocalcium phosphate - $CaH_4(PO_4)_2 \cdot H_2O$ or $CaH_4(PO_4)_2$			
Monsanto Co.			
Monsanto Indust. Chems. Co.	Carondelet, MO		

TABLE C-6 (Continued) PRODUCERS OF CALCIUM PHOSPHATES

Company name	Location of operation (city and state)	Annual capacity (10^3 metric tons)	Remarks
Richardson-Merrell, Inc.			
J. T. Baker Chem. Co., subsid.	Phillipsburg, NJ		
Stauffer Chem. Co.			
Indust. Chem Div.	Nashville, TN		
Calcium phosphate, dibasic (Dicalcium phosphate)			
Tricalcium phosphate - mol ratio of CaO to P_2O_5 ~3 to 1			
Borden Inc.			
Borden Chem. Div.			
Smith-Douglass	Plant City, FL		
Monsanto Co.			
Monsanto Indust. Chems. Co.	Carondelet, MO		
Richardson-Merrell, Inc.			
J. T. Baker Chem Co., subsid.	Phillipsburg, NJ		
Stauffer Chem. Co.			
Indust. Chem. Div.	Chicago Heights, IL		

TABLE C-7. PRODUCERS OF CHLORINE, LIQUID - Cl_2

Company name	Location of operation (city and state)	Annual capacity (10^3 metric tons)	Remarks
The producer of potassium nitrate from potassium chloride and nitric acid necessarily produces chlorine as a by-product.			
Vicksburg Chem. Co.	Vicksburg, MS		

TABLE C-8. PRODUCERS OF DEFLUORINATED PHOSPHATE ROCK*

. Company name	Location of operation (city and state)	Annual capacity (10^3 metric tons)	Remarks
Borden Inc. Borden Chem. Div. Smith-Douglass	Plant City, Fla		
Occidental Petroleum Corp. Hooker Chem. Corp., subsid. Occidental of Florida Div.	White Springs, FL		
Olin Corp. Agricultural Chems. Div.	Pasadena, TX		

---

* usually contains ~30% P_2O_5, <0.2% F

TABLE C-9. PRODUCERS OF FERROPHOSPHOROUS*

No information on producers is available. It can be produced as a co-product of furnace phosphoric acid and of elemental phosphorus.

---

[*] 25 weight percent P, 60 to 70 weight percent Fe, 5 to 15 weight percent others

TABLE C-10. PRODUCERS OF FLUOROSILICIC (HYDROFLUOSILICIC ACID) - H_2SiF_6*

Company name	Location of operation (city and state)	Annual capacity (10^3 metric tons)	Remarks
Burley Belt Chem. Co. Inc.	London, KY		
Chemtech Indust., Inc. Fluoride Mfg. Div.	East St. Louis, IL		
Cities Service Co., Inc. North American Chems. and Metals Group Indust. Chems. Div.	Atlanta, GA		
Essex Chem. Corp. Chems. Div.	Paulsboro, NJ		
Gardinier, Inc. U. S. Phosphoric Products	Tampa, FL		
Gold Kist Inc.	Clyo, GA Cordele, GA		
W. R. Grace & Co. Agricultural Chems. Group	Bartow, FL Columbus, OH Joplin, MO Nashville, TN		
Internat'l Minerals & Chem. Corp. Agricultural Operations Rainbow Div.	Americus, GA Florence, AL Fort Worth, TX Hartsville, SC Spartanburg, SC		
Kaiser Aluminum & Chem. Corp. Kaiser Agricultural Chems. Div.	Riegelwood, NC		

---

*20 to 25 weight percent solution

TABLE C-10 (Continued) PRODUCERS OF FLUOROSILICIC (HYDROFLUOSILICIC ACID) - H_2SiF_6*

Company name	Location of operation (city and state)	Annual capacity (10^3 metric tons)	Remarks
Kewanee Oil Co.			
Harshaw Chem. Co., Div.			
Indust. Chems. Dept.	Cleveland, OH		
Olin Corp.			
Indust. Products and Services Div.	Joliet, IL		
Pelham Phosphate Co.	Pelham, GA		
The Williams Companies			
Agrico Chem. Co., subsid.	Baltimore, MD		
	Pierce, FL		

NOTE: Hydrofluosilicic acid is produced by the action of sulfuric acid on phosphate rock during the manufacture of phosphoric acid (wet process) and phosphate fertilizers. In many cases, it is not recovered. The above is a partial listing only.

* 25 weight percent P, 60 to 70 weight percent Fe, 5 to 15 weight percent others

TABLE C-11. PRODUCERS OF GRANULAR MIXED FERTILIZERS - CONTAIN N, P, AND K

See Directory at the end of this section.

TABLE C-12. PRODUCERS OF GYPSUM - $CaSO_4 \cdot 2H_2O$

Producers of wet-process phosphoric acid necessarily produce gypsum as a by-product. See wet-process phosphoric acid producers since all of these producers may occasionally market gypsum.

TABLE C-13. PRODUCERS OF LIQUID MIXED FERTILIZERS - CONTAIN N, P, AND K

See Directory at the end of this section.

TABLE C-14. PRODUCERS OF LIQUID SUSPENSIONS - CONTAIN N, P, AND K

See Directory at the end of this section.

TABLE C-15. PRODUCERS OF MARKETABLE PHOSPHATE ROCK - AVERAGE OF 31.4 WEIGHT PERCENT P_2O_5

Company name	Location of operation (city and state)	Annual capacity (10^3 metric tons)	Remarks
The following are producers of concentrates, hi-grade crushed rock, and land pebble.			
Beker Indust. Corp Agricultural Products Corp., subsid.	Conda, ID	820	Represents processing capacity; may be expanded. Part leased from Entrada Industries, Inc.
Borden Inc. Borden Chem. Div. Smith-Douglass	Teneroc, FL	680	Teneroc mine may close by 1976
Brewster Phosphates	Bradley, FL	3200	Storage, drying, and grinding at Brewster, FL.
Cominco American Inc.	Garrison, MT	380	
Esmark, Inc. Swift Chem. Co., subsid.	Bartow, FL	n.a.	
	Silver City, FL	1800	Wet products from Watson to to Silver City for additional processing.
	Watson, FL	1550	
Freeport Minerals Co. Freeport Phosphate Rock Co., Div.	Fort Meade, FL	--	See United States Steel Corp. for j. v. with USS Agri-Chemicals, Inc.
Gardinier, Inc. U. S. Phosphoric Products	Fort Meade, FL	1800	
Glacier Natural Products	Polson, MT	n.a.	
W. R. Grace & Co. Agricultural Chems. Group	Bartow, FL	1800	
Internat'l Minerals & Chem. Corp. Agricultural Operations	Achan, FL	--	On stand-by

TABLE C-15 (Continued) PRODUCERS OF MARKETABLE PHOSPHATE ROCK - AVERAGE OF 31.4 WEIGHT PERCENT P_2O_5

Company name	Location of operation (city and state)	Annual Capacity (10^3 metric tons)	Remarks
Agricultural Operations (Cont.)	Clear Springs, FL Kingsford, FL Noralyn, FL	7700	Wet products from Achan & Clear Springs go to Noralyn and/or Kingsford for additional processing. IMC also has facilities for storing & drying rock at E. Tampa and Florida.
Howard Phosphate Co.	Orlando, FL	n.a.	
Kellogg Co.	Ocala, FL	n.a.	
Loncola Phosphate Co.	High Springs, FL	n.a.	
Manko Company, Inc.	Ocala, FL	n.a.	
Meramec Mining Co.	Sullivan, MO	n.a.	
Mobil Oil Corp.			
Mobil Chem. Co., Div. Phosphorus Div.	Nichols, FL	4000	Storage, drying, & grinding at Nichols, FL.
Monsanto Co.			
Monsanto Indus. Chems. Co.	Columbia, TN	1800	Captive use
	Soda Springs, ID	910	Mining is at Henry Mine, ID, 16 miles from Soda Spring, ID
Occidental Petroleum Corp.			
Hooker Chem. Corp., subsid.			
Hooker Chems. & Plastic Corp. subsid.			
Electrochemical & Specialty Chems. Div.	Columbia, TN	550	
Occidental of Florida Div.	White Springs, FL	2700	
Poseidon Mines, Inc.	Lakeland, FL	n.a.	

TABLE C-15 (Continued) PRODUCERS OF MARKETABLE PHOSPHATE ROCK - AVERAGE OF 31.4 WEIGHT PERCENT P_2O_5

Company name	Location of operation (city and state)	Annual capacity (10^3 metric tons)	Remarks
Rocky Mountain Phsophate Co.	Garrison, MT	n.a.	
J. R. Simplot Co. Minerals and Chem. Div.	Conda, ID	550	Low-grade rock is removed to uncover high-grade material at the Gay Mine. FMC Corp. takes the overburden to feed its phosphorus furnaces at Pocatello; part is previously beneficiated at Conda.
	Gay, ID	1600	
Stauffer Chem. Co. Fertilizer and Mining Div.	Crawford Mines (Rich County), UT	730	Utah rock is processed at Leefe, WY
	Leefe, WY	680	
	Vernal, UT	270	
	Wooley Valley, ID	450	Wooley Valley mining is seasonal (summer).
Tennessee Valley Authority	Franklin, TN	110	Rock shipped to TVA furnaces at Muscle Shoals, AL
	Knob Creek, TN	110	
Texasgulf Inc. Agricultural Div.	Aurora, NC	2700	
United States Steel Corp. USS Agri-Chemicals, Div.	Fort Meade, FL	1800	Ft. Meade is a j. v. with Freeport Sulphur Co. who is responsible for half of the total capacity shown.
The Williams Companies Agrico Chem. Co., subsid.	Orange Park, FL Palmetto, FL Payne Creek, FL	6200	
	Total	45,000	

TABLE C-16. PRODUCERS OF NITRIC ACID*

Company name	Location of operation (city and state)	Annual capacity (10^3 metric tons)	Remarks
Agway Inc.	Olean, NY	55	
Air Products and Chems., Inc.	Oyster Creek, TX	36	
	Pensacola, FL	159	
Allied Chem. Corp.			
Indust. Chems. Div.	Buffalo, NY	23	
	Newell, PA	68	
Union Texas Petroleum Div.			
Agricultural Dept.	Geismar, LA	186	
	Omaha, NB	82	
American Cyanamid Co.			
Agricultural Div.	Bound Brook, NJ	23	
	Hannibal, MO	100	
Indust. Chems. and Plastics Div.	Willow Island, WV	27	
Apache Powder Co.	Benson, AZ	55	
Celanese Corp.			
Celanese Chem. Co., Div.	Bay City, TX	68	
CF Indust., Inc.			
Chattanooga Nitrogen Complex	Tyner, TN	155	
Fremont Nitrogen Complex	Fremont, NB	27	
North Carolina Nitrogen Complex	Tunis, NC	310	
Terre Haute Nitrogen Complex	Terre Haute, IN	123	
Coastal States Gas Corp.			
Colorado Interstate Corp., subsid.			
Wycon Chem. Co., sudsid.	Cheyenne, WY	59	
Columbia Nitrogen Corp.	Augusta, GA	145	
	Moultrie, GA	36	
Cominco American Inc.	Beatrice, NB	123	
Commercial Solvents Corp.	Sterlington, LA	150	Captive use
Cooperative Farm Chems. Association	Lawrence, KS	350	
E. I. du Pont de Nemours & Co., Inc.			
Elastomer Chems. Dept.	Beaumont, TX	82	

---

* Usually 52 to 67 weight percent HNO_3 (capacity as 100% HNO_3)

TABLE C-16 (Continued) PRODUCERS OF NITRIC ACID*

Company name	Location of operation (city and state)	Annual capacity (10^3 metric tons)	Remarks
Indust. Chems. Dept.	Gibbstown, NJ	377	
Plastics Dept.	Orange, TX	164	
	Victoria, TX	109	
Polymer Intermediates Dept.	Du Pont, WA	18	
	Louviers, CO	14	
	Seneca, IL.	195	
Textile Fibers Dept.	Old Hickory, TN	41	
Eastman Kodak Co.			
Eastman Chem. Products, Inc., subsid.			
Tennessee Eastman Co., Div.			
Operated for the U. S. Government	Kingsport, TN	95	Operated for U. S. Government
El Paso Natural Gas Co.			
El Paso Products Co., subsid.	Odessa, TX	59	
Gardinier Big River, Inc.	Helena, AK	77	
Goodpasture, Inc.	Dimmitt, TX	n.a.	Small unit for use in nitrogen solution fertilizer manufacture.
W. R. Grace & Co.			
Agricultural Chems. Group	Wilmington, NC	150	
Gulf Oil Corp.			
Gulf Oil Chems. Co., Div.			
Indust. and Specialty Chems. Div.	Pittsburg, KS	255	
Hercules Inc.			
Coatings & Specialty Products Dept.	Parlin, NJ	50	
Indust. Systems Dept.	Bessemer, AL	18	
	Donora, PA	109	
Synthetics Dept.	Hercules, CA	59	
	Louisiana, MO	364	

---

* Usually 52 to 67 weight percent HNO_3 (capacity as 100% HNO_3)

TABLE C-16 (Continued) PRODUCERS OF NITRIC ACID*

Company name	Location of operation (city and state)	Annual capacity (10^3 metric tons)	Remarks
U. S. Army Ordnance Plants, operated by Hercules Inc.	Lawrence, KS	n.a.	Operated for U. S. Government
	Radford, VA	114	Operated for U. S. Government
ICI United States Inc.			
Atlas Aerospace Div.	Tyner, TN	168	Operated for U. S. Government
Illinois Nitrogen Co.	Marseilles, IL	109	
Kaiser Aluminum & Chem. Corp.			
Kaiser Agricultural Chems. Div.	Bainbridge, GA	45	
	North Bend, OH	77	
	Savannah, GA	150	
	Tampa, FL	41	
Lone Star Gas Co.			
Nipak, Inc., subsid.	Kerens, TX	45	
Mississippi Chem. Corp.	Yazoo City, MS	310	
Mobay Chem. Corp.			
Indust. Chems. Div.	Cedar Bayou, TX	45	
	New Martinsville, WV	73	
Mobil Oil Corp.			
Mobil Chem. Co., Div.			
Petrochems. Div.	Beaumont, TX	141	
Monsanto Co.			
Monsanto Agricultural Products Co.	El Dorado, AK	250	
	Luling, LA	250	
Monsanto Textiles Co.	Pensacola, FL	236	
Nitram, Inc.	Tampa, FL	109	
N-Ren Corp.			
Cherokee Nitrogen Div.	Pryor, OK	59	

---

*Usually 52 to 67 weight percent HNO_3 (capacity as 100% HNO_3)

TABLE C-16 (Continued) PRODUCERS OF NITRIC ACID*

Company name	Location of operation (city and state)	Annual capacity (10^3 metric tons)	Remarks
Olin Corp.			
Agricultural Chems. Div.	Lake Charles, LA	150	
Winchester-Western Div.			
Energy Systems Operations			
U. S. Government plants operated by Energy Systems Operations	Baraboo, WI	n.a.	Operated for U.S. Government
	Childersburg, AL	n.a.	Operated for U.S. Government
Phillips Pacific Chem. Co.	Kennewick, WA	41	
Phillips Petroleum Co.			
Fertilizer Div.	Etter, TX	149	
Reichold Chems., Inc.	St. Helens, OR	18	
Rubicon Chems. Inc.	Geismar, LA	136	
St. Paul Ammonia Products, Inc.	Pine Bend, MN	168	
J. R. Simplot Co.			
Minerals and Chem. Div.	Pocatello, ID	n.a.	
Skelly Oil Co.			
Hawkeye Chem. Co., subsid.	Clinton, IA	109	
Standard Oil Co. of California			
Chevron Chem. Co., subsid.			
Ortho Div.	Fort Madison, IA	86	
	Kennewick, WA	123	
	Richmond, CA	77	
The Standard Oil Co. (Ohio)			
Vistron Corp., subsid.			
Chems. Dept.	Lima, OH	59	
Terra Chems. Internat'l, Inc.	Port Neal, IA	114	
Tyler Corp.			
Atlas Powder Co., subsid.	Joplin, MO	114	
	Tamaqua, PA	23	

---

*Usually 52 to 67 weight percent HNO_3 (capacity as 100% HNO_3)

TABLE C-16 (Continued) PRODUCERS OF NITRIC ACID*

Company name	Location of operation (city and state)	Annual capacity (10^3 metric tons)	Remarks
Union Oil Co. of California			
Collier Carbon and Chem. Corp., subsid.	Brea, CA	41	
Uniroyal, Inc.			
United States Ordnance Plant operated by Uniroyal, Inc.	Joliet, IL	177	Operated for U.S. Government
United States Steel Corp.			
USS Agri-Chemicals, Div.	Cherokee, AL	100	
	Crystal City, MO	91	
	Geneva, Utah	73	
Valley Nitrogen Producers, Inc.	El Centro. CA	32	
Vicksburg Chem. Co.	Vicksburg, MS	77	
The Williams Companies			
Agrico Chem. Co., subsid.	Henderson, JY	77	
	Total	8,850	

---

*Usually 52 to 67 weight percent HNO_3 (capacity as 100% HNO_3)

TABLE C-17. PRODUCERS OF NITRIC PHOSPHATE - CONTAINS N, P, AND K

No information is available on producers of nitric phosphate fertilizers.

TABLE C-18. PRODUCERS OF PHOSPHORIC ACIDS, ORTHO*

Company name	Location of operation (city and state)	Annual capacity (10^3 metric tons)	Remarks
Allied Chem. Corp.			
Union Texas Petroleum Div.			
Agricultural Dept.	Geismar, LA	200	Wet
Beker Indust. Corp.			
Agricultural Products Corp., subsid.	Conda, ID	314	Wet
National Phosphate Corp.	Hahnville, LA	270	Wet
	Marseilles, IL	132	Wet
Borden Inc.			
Borden Chem. Div.		207	Wet
Smith-Douglass	Piney Point. FL	207	
	Streator, IL	25	Wet
CF Indust., Inc.			
Bartow Phosphate Complex	Bartow, FL	815	Wet
Plant City Phosphate Complex	Plant City, LF	785	Wet
Engelhard Minerals & Chems. Corp.			
Conserv, Inc., subsid			
Conserv Chems. Div.	Nichols, FL	164	Wet
Farmland Indust., Inc.	Green Bay, FL	595	Wet
First Mississippi Corp.			
FIRST MISS INC., subsid.	Fort Madison, IA	282	Wet
FMC Corp.			
Chem. Group			
Indust. Chem. Div	Carteret, NJ Lawrence, KS Newark, CA	426	Furnace
Freeport Minerals Co.			
Freeport Chem. Co., Div.	Uncle Sam, LA	940	Wet

---

* Usually 75 to 85 weight percent H_3PO_4 (capacity as 100% H_3PO_4)

TABLE C-18 (Continued) PRODUCERS OF PHOSPHORIC ACIDS, ORTHO*

Company name	Location of operation (city and state)	Annual capacity (10^3 metric tons)	Remarks
Gardinier, Inc.			
U. S. Phosphoric Products	Tampa, FL	620	Wet Process
Gardinier Big River, Inc.	Helena, AK	63	Wet
Goodpasture, Inc.	Brownfield, TX	44	Furnace
W. R. Grace & Co.			
Atricultural Chems. Group	Bartow, FL	414	Wet
Hydrite Chem. Co	Milwaukee, WI	10	Furnace
Mississippi Chem. Corp.	Pascagoula, MS	188	Wet; expandable
Mobil Oil Corp.			
Mobil Chem. Co., Div.			
Phosphorus Div.	Carteret, NJ	50	Furnace
	Charleston, SC	23	Furnace
	Depue, IL	150	Wet
	Fernald, OH	44	Furnace
	Gary, IN	23	Furnace
Monsanto Co.			
Monsanto Indust. Chems. Co.	Augusta, GA	56	Furnace
	Carondelet, MO	81	Furnace
	Kearny, NJ	113	Furnace
	Long Beach, CA	100	Furnace
	Trenton, MI	238	Furnace
North Idaho Phosphate Co.	Kellogg, ID	38	Wet
Occidental Petroleum Corp.			
Hooker Chem. Corp., subsid.			
Hooker Chems. and Plastics Corp., subsid.			
Electrochemical and Specialty Chems. Div.	Dallas, TX	56	Furnace
	Godwin, TN	31	Furnace
	Jeffersonville, IN	44	Furnace

---

[*] Usually 75 to 85 weight percent H_3PO_4 (capacity as 100% H_3PO_4)

TABLE C-18 (Continued) PRODUCERS OF PHOSPHORIC ACIDS, ORTHO*

Company name	Location of operation (city and state)	Annual capacity (10^3 metric tons)	Remarks
Occidental of Florida Div.	White Springs, FL	282	Wet
Western Div.	Lathrop, CA	50	Wet
Olin Corp.			
Agricultural Chems. Div.	Pasadena, TX	270	Wet
Indust. Products and Services Div.	Joliet, IL	164	Wet
Pennzoil Co.			
Pennzoil Chem., Inc., subsid.	Hanford, CA	25	Wet
Royster Co.	Mulberry, FL	169	Wet
J. R. Simplot Co.			
Minerals and Chem. Div.	Pocatello, ID	282	Wet
Stauffer Chem. Co.			
Fertilizer and Mining Div.	Pasadena, TX	75	Wet
	Salt Lake City, UT	81	Wet
Indust. Chem. Div.	Chicago, IL	25	Furnace
	Chicago Heights, IL	100	Furnace
	Morrisville, PA	75	Furnace
	Nashville, TN	25	Furnace
	Richmond, CA	25	Furnace
	Silver Bow, MT	25	Furnace
	South Gate, CA	44	Furnace
Tennessee Valley Authority	Muscle Shoals, AL	106	Furnace
Texasgulf Inc.			
Agricultural Div.	Aurora, NC	640	Wet
Union Oil Co. of California			
Collier Carbon & Chem. Corp., subsid.	Nichols, CA	10	
United States Steel Corp.			
USS Agri-Chemicals, Div.	Bartow, FL	113	Wet
	Fort Meade, FL	226	Wet

---

*Usually 75 to 85 weight percent H_3PO_4 (capacity as 100% H_3PO_4)

TABLE C-18 (Continued) PRODUCERS OF PHOSPHORIC ACIDS, ORTHO*

Company name	Location of operation (city and state)	Annual capacity (10^3 metric tons)	Remarks
Valley Nitrogen Producers, Inc.	Helm, CA	58	Wet
AFC Co., subsid.	Bena, CA	9	
The Williams Companies			
Agrico Chem. Co., subsid.	Donaldsonville, LA	500	Wet
	Pierce, FL	350	Wet
	Total	11,300	

---

[*] Usually 75 to 85 weight percent H_3PO_4 (capacity as 100% H_3PO_4)

TABLE C-19. PRODUCERS OF PHOSPHORIC ACIDS, SUPER*

Company name	Location of operation (city and state)	Annual capacity (10^3 metric tons)	Remarks
Allied Chem. Corp.			
Union Texas Petroleum Div.			
Agricultural Dept.	Geismar, LA	159	Wet/submerged combustion
Engelhard Minerals & Chems. Corp.			
Conserv. Inc., subsid.			
Conserv Chems. Div.	Nichols, FL	n.a.	
Farmland Indust., Inc.	Green Bay, FL	173	Wet/vacuum
FMC Corp.			
Chem. Group			
Indust. Chem. Div.	Carteret, NJ	n.a.	Furnace; superphosphoric acids produced occasionally at Carteret, Lawrence, and Newark
	Lawrence, KS	n.a.	
	Newark, CA	n.a.	
Goodpasture, Inc.	Brownfield, TX	44	Furnace; not currently operating
Internat's Minerals & Chem. Corp.			
Agricultural Operations	Bonnie, FL	226	Wet/vacuum; acid is rediluted and used captively to make feed phosphates.
North Idaho Phosphate Co.	Kellogg, ID	14	Wet/vacuum
Occidental Petroleum Corp.			
Hooker Chem. Corp., subsid.			
Occidental of Florida Div.	White Springs, FL	150	Wet/staff
J. R. Simplot Co.			
Minerals and Chem. Div.	Pocatello, ID	69	Wet/vacuum
Stauffer Chem. Co.			
Fertilizer and Mining Div.	Pasadena, TX	28	Wet/vacuum
	Salt Lake City, UT	43	Wet vacuum

---

* Usually 105 weight percent H_3PO_4 (capacity as 100% H_3PO_4)

TABLE C-19 (Continued) PRODUCERS OF PHOSPHORIC ACIDS, SUPER*

Company name	Location of operation (city and state)	Annual capacity (10^3 metric tons)	Remarks
Indust. Chem. Div.	Chicago, IL Richmond, CA Silver Bow, MT	n.a. n.a.	Furnace; superphosphoric acids produced occasionally at Chicago, Richmond, and Silver Bow.
Tennessee Valley Authority	Muscle Shoals, AL	106	Furnace
Texasgulf Inc. Agricultural Div.	Aurora, NC	311	Wet/vacuum
	Total	1,320	

---

*Usually 105 weight percent H_3PO_4 (capacity as 100% H_3PO_4)

TABLE C-20. PRODUCERS OF PHOSPHOROUS, ELEMENTAL - P_4

Company name	Location of operation (city and state)	Annual capacity (10^3 metric tons)	Remarks
Electro-Phos Corp.	Pierce, FL	10	
FMC Corp.			
Chem. Group			
Indust. Chem. Div.	Pocatello, ID	118	
Mobil Oil Corp.			
Mobil Chem. Co., Div.			
Phosphorus Div.	Nichols, FL	5	
Monsanto Co.			
Monsanto Indust. Chems. Co.	Columbia, TN	111	
	Soda Springs, ID	100	
Occidental Petroleum Corp.			
Hooker Chem. Corp., subsid.			
Hooker Chems. and Plastics Corp., subsid.			
Electrochemical and Specialty Chems. Div.	Columbia, TN	55	
Stauffer Chem. Co.			
Indust. Chem. Div.	Mt. Pleasant, TN	41	
	Silver Bow, MT	38	
	Tarpon Springs, FL	21	
Tennessee Valley Authority	Muscle Shoals, AL	23	
	Total	511	

NOTE: Capacities are on a P_4 basis.

TABLE C-21. PRODUCERS OF PHOSPHOROUS, PENTOXIDE - P_2O_5

Company name	Location of operation (city and state)	Annual capacity (10^3 metric tons)	Remarks
Occidental Petroleum Corp. Hooker Chem. Corp., subsid. Hooker Chems. and Plastics Corp., subsid. Electrochemical and Specialty Chems. Div.	Niagara Falls, NY		
Stauffer Chem. Co. Indust. Chem. div.	Morrisville, PA Nashville, TN.		
Texasgulf Inc. Agricultural Div.	Aurora, NC		

TABLE C-22. PRODUCERS OF POTASSIUM NITRATE - 95% KNO_3

Company name	Location of operation (city and state)	Annual capacity (10^3 metric tons)	Remarks
Vicksburg Chem. Co.	Vicksburg, MS		

TABLE C-23. PRODUCERS OF SLAG*

Producers of furnace phosphoric acid necessarily produce slag as a by-product. See furnace orthophosphoric and superphosphoric acid producers since all of these may market slag.

---

* ~50 weight percent CaO, ~40 weight percent SiO_2, ~10% other oxides.

TABLE C-24. PRODUCERS OF SODIUM ORTHOPHOSPHATES AND POLYPHOSPHATES*

Company name	Location of operation (city and state)	Annual capacity (10^3 metric tons)	Remarks
Essex Chem. Corp. Chems. Div.	Rumford, RI		Sodium hexametaphosphate Sodium metaphosphate Sodium tetraphosphate
FMC Corp. Chem. Group Indust. Chem. Div.	Carteret, NJ	91[a]	Disodium phosphate Monosodium phosphate Sodium acid pyrophosphate Sodium hexametaphosphate Sodium tetraphosphate Sodium tripolyphosphate Tetrasodium pyrophosphate Trisodium phosphate monohydrate and crystals
	Green River, WY	68[a]	Sodium tripolyphosphate
	Lawrence, KS		Disodium phosphate Monosodium phosphate Sodium acid pyrophosphate Sodium hexametaphosphate Sodium tetraphosphate

---

* Na_2HPO_4; NaH_2PO_4; Na_3PO_4; $Na_2H_2P_2O_7$; $Na_4P_2O_7$; $Na_5P_3O_{10}$.

TABLE C-24 (Continued) PRODUCERS OF SODIUM ORTHOPHOSPHATES AND POLYPHOSPHATES*

Company name	Location of operation (city and state)	Annual capacity (10^3 metric tons)	Remarks
FMC Corp. (continued)		68[a]	Sodium tripolyphosphate Tetrasodium pyrophosphate Trisodium phosphate, monohydrate and crystals Disodium phosphate Monosodium phosphate Sodium acid pyrophosphate Sodium hexametaphosphate Sodium tetraphosphate
		45[a]	Sodium tripolyphosphate Tetrasodium pyrophosphate Trisodium phosphate, monochydrate and crystals
Heico, Inc.	Delaware Water Gap, PA		Monosodium phosphate
Mallinckrodt, Inc. Indust. Chems. Div.	St. Louis, MO		Monosodium phosphate Trisodium phosphate
Merck & Co., Inc. Calgon Corp., subsid. Consumer Products Co., Inc., Div.	Morrisville, PA		Sodium hexametaphosphate
	Rockwood, MI		Sodium hexametaphosphate Sodium metaphosphate
Mobil Oil Corp. Mobil Chem. Co., Div. Phosphorus Div.	Carteret, NJ[b]	45[a]	Sodium tripolyphosphate Trisodium phosphate
	Fernald, OH	45[a]	Sodium tripolyphosphate
Monsanto Co. Monsanto Indust. Chems. Co.	Augusta, GA	50[a]	Sodium tripolyphosphate Sodium aluminum phosphate
	Carondelet, MO	91[a]	Sodium tripolyphosphate Trisodium phosphate, anhydrous

---

* Na_2HPO_4; NaH_2PO_4; Na_3PO_4; $Na_2H_2P_2O_7$; $Na_4P_2O_7$; $Na_5P_3O_{10}$.

TABLE C-24 (Continued) PRODUCERS OF SODIUM ORTHOPHOSPHATES AND POLYPHOSPHATES*

Company name	Location of operation (city and state)	Annual capacity (10^3 metric tons)	Remarks
Monsanto Co. (continued)	Kearny, NJ	114[a]	Sodium tripolyphosphate
	Long Beach, CA	68[a]	Sodium tripolyphosphate
	Trenton, MI		Disodium phosphate, anhydrous and dihydrate
			Monosodium phosphate
			Sodium acid pyrophosphate
			Sodium hexametaphosphate
			Sodium metaphosphate insoluble
		68[a]	Sodium tripolyphosphate
			Tetrasodium pyrophosphate
			Trisodium phosphate, crystalline
Occidental Petroleum Corp. Hooker Chem. Corp., subsid. Hooker Chems. & Plastics Corp., subsid. Electrochemical & Specialty Chems. Div.	Dallas, TX	32[a]	Sodium tripolyphosphate, anhydrous
	Jeffersonville, IN		Disodium phosphate, anhydrous
			Sodium hexametaphosphate
		91[a]	Sodium tripolyphosphate, anhydrous
			Trisodium phosphate, anhydrous and crystalline
Olin Corp. Indust. Products & Services Div.	Joliet, IL		Disodium phosphate, anhydrous and crystalline
			Monosodium phosphate, anhydrous
			Monosodium phosphate monohydrate

---

* Na_2HPO_4; NaH_2PO_4; Na_3PO_4; $Na_2H_2P_2O_7$; $Na_4P_2O_7$; $Na_5P_3O_{10}$

TABLE C-24 (Continued) PRODUCERS OF SODIUM ORTHOPHOSPHATES AND POLYPHOSPHATES*

Company name	Location of operation (city and state)	Annual capacity (10^3 metric tons)	Remarks
Olin Corp. (continued)		127^a	Sodium acid pyrophosphate Sodium hexametaphosphate Sodium metaphosphate Sodium tetraphosphate Sodium tripolyphosphate, anhydrous and hydrated Tetrasodium pyrophosphate, anhydrous Trisodium phosphate, anhydrous chlorinated, and crystalline Trisodium phosphate monohydrate
Stauffer Chem. Co. Indust. Chem. Div.	Chicago, IL	36^a	Sodium tripolyphosphate, anhydrous Sodium metaphosphate
	Chicago Heights, IL		Disodium phosphate, anhydrous Disodium phosphate, duohydrate Monosodium phosphate, anhydrous Sodium acid pyrophosphate Sodium iron pyrophosphate Sodium potassium aluminum phosphate Sodium trimetaphosphate Tetrasodium pyrophosphate, anhydrous Trisodium phosphate, anhydrous Trisodium phosphate, dodecahydrate & chlorinated

---

[*] Na_2HPO_4; NaH_2PO_4; Na_3PO_4; $Na_2H_2P_2O_7$; $Na_4P_2O_7$; $Na_5P_3O_{10}$

TABLE C-24 (Continued) PRODUCERS OF SODIUM ORTHOPHOSPHATES AND POLYPHOSPHATES*

Company name	Location of operation (city and state)	Annual capacity (10^3 metric tons)	Remarks
Stauffer Chem. Co. (continued)	Morrisville, PA		Sodium hexametaphosphate
			Sodium metaphosphate, insoluble
		68[a]	Sodium tripolyphosphate
			Trisodium phosphate, chlorinated
	Richmond, CA		Trisodium phosphate, chlorinated
	South Gate, CA		Disodium phosphate, anhydrous
			Monosodium phosphate, anhydrous
			Sodium acid pyrophosphate, anhydrous
			Tetrasodium pyrophosphate, anhydrous
			Trisodium phosphate, anhydrous
			Trisodium phosphate, dodecahydrate
	Total	1,110[a]	

---

[a] Capacities are for sodium tripolyphosphate.
[b] On stand-by.

NOTE: Capacities are meant to be relative, since they vary widely depending on density of various tripolyphosphates produced; further, most facilities can make other phosphates as well.

[*] Na_2HPO_4; NaH_2PO_4; Na_3PO_4; $Na_2H_2P_2O_7$; $Na_4P_2O_7$; $Na_5P_3O_{10}$

TABLE C-25. PRODUCERS OF SULFURIC ACID*

Company name	Location of operation (city and state)	Annual capacity (10^3 metric tons)	Remarks
Allied Chem. Corp.			
Indust. Chems. Div.	Anacortes, WA	73	Elemental
	Baton Rouge, LA	91	Elemental
	Buffalo, NY	177	Elemental
	Chicago, IL	145	Elemental
	Cleveland, OH	118	Elemental
	East St. Louis, IL	173	Elemental
	Elizabeth, NJ	182	Elemental
	Front Royal, VA	145	Elemental
	Geismar, LA	455	Elemental
	Hopewell, VA	182	Elemental; may be expanded
	Nitro, WV	127	Elemental
	Pittsburg, CA	127	Elemental
American Cyanamid Co.			
Indust. Chems. & Plastics Div.	Hamilton, OH	82	Elemental
	Joliet, IL	45	Elemental
	Kalamazoo, MI	23	Elemental
	Linden, NJ	218	Elemental
	New Orleans, LA	50	Elemental
	Savannah, GA	205	Elemental
Organic Chems. Div.	Bound Brook, NJ	59	Elemental
	Wead Heights, NV	127	Elemental, may be closed
Beker Indust. Corp.			
Agricultural Products Corp., subsid.	Conda, ID	545	Elemental
National Phosphate Corp., subsid.	Hahnville, LA	464	Elemental
	Marsailles, IL	232	Elemental

---

[*] 93 to 98 weight percent H_2SO_4 (capacities as 100% H_2SO_4)

TABLE C-25 (Continued) PRODUCERS OF SULFURIC ACID*

Company name	Location of operation (city and state)	Annual capacity (10^3 metric tons)	Remarks
Borden, Inc.			
Borden Chem. Div.			
Smith-Douglass	Chesapeake, VA	73	Elemental
	Piney Point, FL	445	Elemental
	Streator, IL	36	Elemental
CF Indust. Inc.			
Bartow Phosphate Complex	Bartow, FL	1,545	Elemental
Plant City Phosphate Complex	Plant City, FL	1,455	Elemental
Cities Service Co., Inc.			
Columbian Div.	Monmouth Junction, NJ	32	
North American Chems. & Metals Group			
Indust. Chems. Div.	Augusta, GA	118	Elemental
Climax Chem. Co.	Monument, NM	68	Elemental
Columbia Nitrogen Corp.	Moultrie, GA	18	Elemental; may be closed
Commonwealth Oil Refining Co., Inc.	Penuelas, PR	27	Elemental
Cyprus Mines Corp.			
Cyprus Bagdad Copper Co.	Bagdad, AZ	45	Elemental
Delta Chems., Inc.	Searsport, ME	68	Elemental
Detroit Chem. Works			
Pressure Vessel Services, Div.	Detroit, MI	32	Elemental
E. I. du Pont de Nemours & Co., Inc.			
Biochems. Dept.	La Porte, TX	318	Elemental
Indust. Chems. Dept.	Burnside, LA	464	Elemental
	Cleveland, OH	195	Elemental
	Corwells Heights, PA	64	Elemental
	East Chicago, IN	341	Elemental
	Gibbstown, NJ	100	Elemental

---

* 93 to 98 weight percent H_2SO_4 (capacities as 100% H_2SO_4)

TABLE C-25 (Continued) PRODUCERS OF SULFURIC ACID*

Company name	Location of operation (city and state)	Annual capacity (10^3 metric tons)	Remarks
Indust. Chems. Dept. (cont.)	Linden, NJ	295	Elemental
	North Bend, OH	159	Elemental
	Richmond, VA	86	Elemental
	Wurtland, KY	182	Elemental
Organic Chems. Dept.			
Dyes and Chems. Div.	Deepwater, NJ	82	Elemental
Polymer Intermediates Dept.	Newport, IN	115	Elemental; operated for U.S. Government
Eagle-Picher Indust., Inc.			
Agricultural Chems. Div.	Galena, KS	136	Elemental; on stand-by
Eastman Kodak Co.			
Eastman Chem. Products, Inc.,subsid.			
DPI Div.	Rochester, NY	5	Elemental; captive use
El Paso Acid Corp.	El Paso, TX	77	Elemental
Engelhard Minerals & Chems. Corp.			
Conserv, Inc., subsid			
Conserv Chems. Div.	Nichols, FL	364	Elemental
National Zinc Co., subsid.	Bartlesville, OK	82	Elemental
Esmark, Inc.			
Swift Chem. Co., subsid.	Bartow, FL	n.a.	
	Calumet City, IL	n.a.	
	Dothan, AL	27	Elemental
	Norfolk, VA	55	Elemental
	Wilmington, NC	45	Elemental
Essex Chem. Corp.			
Chems. Div.	Newark, NJ	164	Elemental
Farmland Indust., Inc.	Green Bay, FL	1,180	Elemental

---

* 93 to 98 weight percent H_2SO_4 (capacities as 100% H_2SO_4)

TABLE C-25 (Continued) PRODUCERS OF SULFURIC ACID*

Company name	Location of operation (city and state)	Annual capacity (10^3 metric tons)	Remarks
First Mississippi Corp. FIRST MISS INC., subsid.	Fort Madison, IA	464	Elemental
Freeport Minerals Co. Freeport Chem. Co., Div.	Port Sulphur, LA	n.a.	
	Uncle Sam, LA	2,025	Elemental
Gardinier, Inc. U. S. Phosphoric Products	Tampa, FL	1,360	Elemental
Gardinier Big River, Inc.	Helena, AR	136	Elemental
Georgia-Pacific Corp. Chem. Div.	Bellingham, WA	18	Elemental
W. R. Grace & Co. Agricultural Chems. Group	Bartow, FL	770	Elemental
	Charleston, SC	36	Elemental; may be closed
	Joplin, MO	n.a.	
Gulf + Western Indust., Inc. The New Jersey Zinc Co., subsid.	Palmerton, PA	145	Elemental
Kerr-McGee Corp. Kerr-McGee Chem. Corp., subsid.	Grants, NM	64	Elemental
	Cottondale, FL	27	Elemental
L. J. & M. La Place Co.	Edison, NJ	64	
Minnesota Mining and MFg. Co. Chem. Resources Div.	Copley, OH	55	Elemental
Mississippi Chem. Corp.	Pascagoula, MI	905	Elemental
Mobil Oil Corp. Mobil Chem. Co., Div. Phosphorus Div.	Depue, IL	380	Elemental

---

[*] 93 to 98 weight percent H_2SO_4 (capacities as 100% H_2SO_4)

TABLE C-25 (Continued) PRODUCERS OF SULFURIC ACID*

Company name	Location of operation (city and state)	Annual capacity (10^3 metric tons)	Remarks
Monsanto Co.			
Monsanto Agricultural Products Co.	El Dorado, AR	159	Elemental
Monsanto Indust. Chems. Co.	Avon, CA	123	Elemental
	Everett, MA	86	Elemental
	Sauget, IL	309	Elemental
National Distillers & Chem. Corp.			
Chems. Div.			
U.S. Indust. Chems. Co., Div.	De Soto, KS	91	Elemental
	Dubuque, IA	64	Elemental
N L Indust., Inc.			
Titanium Pigment Div.	St. Louis, MO	270	Elemental
	Sayreville, NJ	545	Elemental
N-Ren Corp.			
North Star Div.	Pine Bend, MN	109	Elemental; may be closed
Occidental Petroleum Corp.			
Hooker Chem. Corp., subsid.			
Occidental Chem. Co., subsid.			
Southern Region	Plainview, TX	91	Elemental
Occidental of Florida Div.	White Springs, FL	636	Elemental
Western Div.	Lathrop, CA	205	Elemental
Olin Corp.			
Agricultural Chems. Div.	Pasadena, TX	432	Elemental
Indust. Products & Services Div.	Baltimore, MD	270	Elemental
	North Little Rock, AR	82	Elemental
	Paulsboro, NJ	209	Elemental
	Shreveport, LA	127	Elemental

---

* 93 to 98 weight percent H_2SO_4 (capacities as 100% H_2SO_4)

TABLE C-25 (Continued) PRODUCERS OF SULFURIC ACID*

Company name	Location of operation (city and state)	Annual capacity (10^3 metric tons)	Remarks
Pennwalt Corp. Ozark-Mahoning Co., subsid.	Tulsa, OK	109	
Phelps-Dodge Corp. Western Nuclear, Inc., subsid.	Jeffrey City, WY	32	Elemental
	Riverton, WY	68	
Reichold Chems., Inc.	Tuscaloosa, AL	68	Elemental; may be closed
Rohm and Haas Co.	Philadelphia, PA	82	Elemental; may be closed
Royster Co.	Chesapeake, VA	18	Elemental; may be closed
	Mulberry, FL	320	Elemental
J. R. Simplot Co. Mineral and Chem. Div.	Pocatello, ID	730	Elemental; output cut back
Southern States Phosphate and Fertilizer Co.	Savannah, GA	32	Elemental
Standard Oil Co. (Indiana) Amoco Oil Co., subsid.	Texas City, TX	159	Elemental
Stauffer Chem. Co. Fertilizer and Mining Div.	Pasadena, TX	409	Elemental
Indust. Chem. Civ.	Baton Rouge, LA	680	Elemental
	Bay Town, TX	250	Elemental
	Dominguez, CA	295	Elemental
	Forth Worth, TX	109	Elemental
	Hammond, IN	250	Elemental
	Le Moyne, AL	191	Elemental
	Manchester, TX	1,270	Elemental
	Martinez, CA	227	Elemental

---

* 93 to 98 weight percent H_2SO_4 (capacities as 100% H_2SO_4)

TABLE C-25 (Continued) PRODUCERS OF SULFURIC ACID*

Company name	Location of operation (city and state)	Annual capacity (10^3 metric tons)	Remarks
Texasgulf Inc. Agricultural Div.	Aurora, NC	2,020	Elemental
Union Carbide Corp. Chems. and Plastics Div.	Texas City, TX	n.a.	
Union Oil Co. of California Collier Carbon & Chem. Corp., subsid.	Wilmington, CA	127	Elemental
United States Steel Corp. USS Agri-Chemicals, Div.	Bartow, FL	264	Elemental
	Fort Meade, FL	491	Elemental
	Wilmington, NC	86	Elemental; may be closed
USS Chems., Div.	Neville Island, PA	45	Elemental
Valley Nitrogen Producers, Inc.	Helm, CA	225	Elemental
AFC Co., subsid.	Bena, CA	64	
Weaver Fertilizer Co., Inc.	Norfolk, VA	45	Elemental
The Williams Companies Agrico Chem. Co., subsid.	Baltimore, MD	23	
	Bay City, MI	36	
	Cairo, OH	n.a.	
	Pierce, FL	636	
Wright Chem. Corp.	Acme, NC	54	Elemental
	Total		

---

* 93 to 98 weight percent H_2SO_4 (capacities as 100% H_2SO_4)

TABLE C-26. PRODUCERS OF SUPERPHOSPHATE, NORMAL - 18 TO 20 WEIGHT PERCENT P_2O_5

Company name	Location of operation (city and state)	Annual capacity (10^3 metric tons)	Remarks
Alabama Farmers Cooperative, Inc.	Selma, AL	n.a.	
American Plant Food Corp.	Galena Park, TX	n.a.	
Borden Inc. Borden Chemical Division Smith-Douglass	Norfolk, VA	n.a.	
	Streator, IL	n.a.	0-26-0
Columbia Nitrogen Corp.	Moultrie, GA	104	
Esmark, Inc. Swift Chemicals Co. Operation	Bartow, FL	100	
	Birmingham, AL	200	
	Charleston, SC	182	
	Dothan, AL	232	
	Norfolk, VA	200	
	Savannah, Georgia	63	
	Wilmington, NC	166	
Gardinier, Inc. U. S. Phosphoric Products	Tampa, FL	200	
Gold Kist, Inc.	Clyo, GA	133	
	Cordele, GA	133	
W. R. Grace & Co. Agricultural Chemicals Group	Charleston, SC	n.a.	These are N-P-K plants capable of producing normal superphosphate
	Columbus, OH	n.a.	
	Joplin, MI	n.a.	
	Nashville, TN		
Indiana Farm Bureau Cooperative Association, Inc.	Indianapolis, IN	133	
Internat'l Minerals & Chem. Corp. Agricultural Operations Rainbow Division	Americus, GA	76	
	Florence, AL	133	
	Fort Worth, TX	133	
	Hartsville, SC	133	
	Spartanburg, SC	133	

TABLE C-26 (Continued) PRODUCERS OF SUPERPHOSPHATE, NORMAL - 18 TO 20 WEIGHT PERCENT P_2O_5

Company name	Location of operation (city and state)	Annual capacity (10^3 metric tons)	Remarks
Kaiser Aluminum & Chem. Corp.			
Kaiser Agricultural Chem. Div.	Acme, NC	200	
Kerr-McGee Corp.			
Kerr-McGee Chem. Corp., subsid.	Baltimore, MD	166	
	Cottondale, FL	166	
	Jacksonville, FL	166	
	Philadelphia, PA	166	
Layco Chem. Co.	Pierce, FL	66	
Lone Star Gas Co.			
Nipak, Inc., subsid.	Littlefield, TX	46	
Mineral Fertilizer Co.	North Salt Lake, UT	n.a.	
Occidental Petroleum Corp.			
Occidental Chem. Co., subsid.			
Western Div.	Lathrop, CA	131	
Richmond Guano Co.	Richmond, VA	53	
Royster Co.	Athens, GA	46	
	Chesapeake, VA	100	
Southeast Chem. Co. Inc.	London, KY	80	
Southern States Phosphate and Fertilizer Co.	Savannah, GA	n.a.	
Stauffer Chemical Co.			
Fertilizer and Mining Div.	Tacoma, WA	100	
Texaco Inc.			
Federal Chem. Co., subsid.	Columbus, OH	n.a.	
	Nashville, TN	n.a.	May be closed
	Omaha, NB	n.a.	May be closed
	Total	5,100	

TABLE C-27. PRODUCERS OF SUPERPHOSPHATE, TRIPLE - 46 WEIGHT PERCENT P_2O_5

Company name	Location of operation (city and state)	Annual capacity (10^3 metric tons)	Remarks
Borden Inc.			
Borden Chemical Div.			
Smith-Douglass	Piney Point, FL	64	
CF Industries, Inc.			
Plant City Phosphate Complex	Plant City, FL	482	
Conserv, Inc.			
Conserv Chemicals Div.	Nichols, FL	255	Low stream factor
Farmland Industries, Inc.	Green Bay, FL	173	
Gardinier, Inc.			
U.S. Phosphoric Products	Tampa, FL	677	
W. R. Grace & Co.			
Agricultural Chem. Group	Bartow, FL	605	Includes one train that also produces ammonium phosphates
	Joplin, MO	91	
Mississippi Chem. Corp.	Pascagoula, MS	270	
Occidental Petroleum Corp.			
Occidental Chem. Co., subsid.			
Occidental of Florida Div.	White Springs, FL	420	Two trains, one of which may produce ammonium phosphate
Royster Co.	Mulberry, FL	191	
J. R. Simplot Co.			
Minerals and Chem. Div.	Pocatello, ID	109	
Stauffer Chemical Co.			
Fertilizer and Mining Div.	Salt Lake City, UT	32	
Texasgulf, Inc.			
Agricultural Div.	Aurora, NC	336	
	Total	4,520	

NOTE: Capacities are for gross weight. Some of these plants produce ammonium phosphatea and N-P-K products as well as triple superphosphate in the same equipment.

TABLE C-28. PRODUCERS OF UREA - NH_2CONH_2

Company name	Location of operation (city and state)	Annual capacity (10^3 metric tons)	Remarks
Agway Inc.	Olean, NY	54	
Air-Products and Chems., Inc.	Pensacola, FL	23	
Allied Chem. Corp.			
Specialty Chems. Div.	South Point, OH	64	May be closed
Union Texas Petroleum Div.			
Agricultural Dept.	Geismar, LA	205	
	Omaha, NB	127	
American Cyanamid Co.			
Agricultural Div.	New Orleans, LA	132	
Borden Inc.			
Borden Chem. Div.			
Petrochems. Div.	Geismar, LA	177	
CF Indust., Inc.			
Chattanooga Nitrogen Complex	Tyner, TN	36	
Donaldsonville Nitrogen Complex	Donaldsonville, LA	332	
Fremont Nitrogen Complex	Fremont, NB	18	
North Carolina Nitrogen Complex	Tunis, NC	155	
Coastal States Gas Corp.			
Colorado Interstate Corp., subsid.			
Wycon Chem. Co., subsid.	Cheyenne, WY	45	
Columbia Nitrogen Corp.	Augusta, GA	27	
Cooperative Farm Chems. Association	Lawrence, KS	182	
Gardinier Big River, Inc.	Helena, AR	59	
Gen. American Oil of Texas			
Premier Petrochem. Co., subsid.	Pasadena, TX	95	
Goodpasture, Inc.	Dimmit, TX	23	
W. R. Grace & Co.			
Agricultural Chems. Group	Memphis, TN	123	
Hercules Inc.			
Synthetics Dept.	Hercules, CA	36	
	Louisiana, MO	86	

TABLE C-28 (Continued) PRODUCERS OF UREA - NH_2CONH_2

Company name	Location of operation (city and state)	Annual capacity (10^3 metric tons)	Remarks
Kaiser Aluminum & Chem. Corp.			
Kaiser Agricultural Chems. Div.	Savannah, GA	73	
Lone Star Gas Co.			
Nipak, Inc., subsid.	Kerens, TX	77	
	Pryor, OK	123	
Mississippi Chem. Corp.	Yazoo City, MS	168	
Mobil Oil Corp.			
Mobil Chem. Co., Div.			
Petrochem. Div.	Beaumont, TX	45	
N-Ren Corp.			
Cherokee Nitrogen Div.	Pryor, OH	18	
High Plains Div.	Plainview, TX	55	
Olin Corp.			
Agricultural Chems. Div.	Lake Charles, LA	145	
Phillips Pacific Chem. Co.	Kennewick, WA	41	
Phillips Petroleum Co.			
Fertilizer Div.	Beatrice, NB	50	
Reichold Chems., Inc.	St. Helens, OR	50	
St. Paul Ammonia Products, Inc.	East Dubuque, IL	73	
J. R. Simplot Co.			
Minerals and Chem. Div.	Pocatello, ID	n.a.	
Skelly Oil Co.			
Hawkeye Chem. Co., subsid.	Clinton, IA	54	
The Standard Oil Co. (Ohio)			
Vistron Corp., subsid.			
Chems. Dept.	Lima, OH	218	
Tennessee Valley Authority	Muscle Shoals, AL	64	
Terra Chems. Internat'l, Inc.	Port Neal, IA	155	
Triad Chem.	Donaldsonville, LA	42	

TABLE C-28 (Continued) PRODUCERS OF UREA - NH_2CONH_2

Company name	Location of operation (city and state)	Annual capacity (10^3 metric tons)	Remarks
Tyler Corp.			
Atlas Powder Co., subsid.	Joplin, MO	59	
Union Oil Co. of California			
Collier Carbon and Chem. Corp., subsid.	Brea, CA	50	
	*Kenai, AK	309	
United States Steel Corp.			
USS Agri-Chemicals, Div.	Cherokee, AL	23	
Valley Nitrogen Producers, Inc.	El Centro, CA	141	
	Helm, CA	32	
The Williams Companies			
Agrico Chem. Co., subsid.	Blytheville, AR	300	
	Donaldsonville, LA	300	
	Total	5,060	

---

[*] Joint venture with Mitsubishi Gas Chemical Co.

APPENDIX D

FERTILIZER INDUSTRY BIBLIOGRAPHY

BIBLIOGRAPHIES

Available from the Technical Library

I. RAW MATERIALS

Number	Subject	No. of Refs.	Period
1062	Open-Pit Mining of Phosphate Rock	19	1959-1968
1085	Phosphate Rock: Mining and Beneficiation	90	1944-1968
1117	Sulfur: Ore Deposits and Extraction Processes	22	1954-1968
1137	Fertilizer Raw Materials: Sources of Information	16	Compiled 1967
1144	Sulfur Extraction from Pyrites	7	1962-1966
1164	Bacteriological Digestion of Gypsum as a Source for Sulfur	13	1931-1969
1214	Minor Elements in Phosphate Rock	52	1924-1968
1283	World-Wide Phosphate Reserves	91	Compiled 1975
1296	Organic Matter in Phosphate Rock	9	Compiled 1972
1392	Phosphate Rock - Florida	40	1970-1973
1418	Substitution of Al or S for P in Apatites	18	1938-1974
1433	Uranium in Phosphate Rock	60	1947-1974
1477	Potash Deposits	85	1967-1975

II. MANUFACTURING PROCESSES AND MATERIALS

Number	Subject	No. of Refs.	Period
1004	Suspension Fertilizer	111	1962-1970
1027	Bulk-Blending of Fertilizers	106	1958-1975
1120	Selected Bibliography on Fertilizers, with Source and Price	109	Compiled 1974
1120A	Fertilizers, Selected Periodical List with Source and Price	59	Compiled 1974
1131	Plant Food Losses in Fertilizer Production	12	1952-1968
1156	Spherodizing Fertilizers	7	1959-1970
1162	Hydrogen by Electrolysis of Water	72	1958-1973
1180	Plant Production of NPK Fertilizers	6	1960-1969
1219	Manufacture of Calcium Carbonate from Calcium Nitrate	5	1933-1970
1249	Fertilizer Granulation Processes	160	1951-1975
1331	Granulation of Lime and Limestone	16	Compiled 1972
1346	Fertilizers of Low Bulk Density	10	Compiled 1973
1368	Energy Requirements for the Production of N, P, and K Fertilizers	93	Compiled 1973
1428	Quality Control in Fertilizer Manufacture	132	Compiled 1974
1442	Use of Surfactants in Fertilizer Manufacture	40	1966-1974
1469	History of Fertilizers: Manufacture & Use	40	Compiled 1975
1492	Publications on Safety in Production, Handling & Storage of Fertilizers	44	Compiled 1976

IIA. Phosphorus Compounds

Number	Subject	No. of Refs.	Period
1001	Ammoniated Phosphates - Manufacture, Patents & Use	284	Compiled 1973
1007	Purification of Phosphoric Acid	176	1957-1972
1019	Reactions of Ammonia and P_2O_5	41	Compiled 1973
1023	Nitric Phosphates: Manufacture and Use	237	1951-1975
1030	Acidulation of Phosphate Rock with HCl	42	1957-1974
1044	Treatment and Disposal of Phosphate Slimes	42	1949-1974

Preceding page blank

Number	Subject	No. of Refs.	Period
	IIA. Phosphorus Compounds (Continued)		
1045	Solubility of Metal Complexes in Phosphoric Acid	13	1957-1969
1047	Reaction of Phosphate Rock and Fluosilicate	17	1964-1970
1055	Defluorination of Phosphate Rock	118	Compiled 1975
1063	Liquid Fertilizers Using Wet-Phosphoric Acid	41	1959-1970
1067	Ammonium Polyphosphates	137	1952-1972
1127	Ammonium Phosphate by the Reaction of HCl and H_3PO_4	5	1959-1965
1145	Potassium Hydroxide in Fertilizer Manufacture	8	1955-1965
1148	Defluorination of Wet Phosphoric Acid	37	1957-1974
1157	The Manufacture of Wet-Process H_3PO_4 from Igneous Apatite	20	1955-1969
1163	The Production of H_3PO_4 with the Process of Acidulation of Phosphate Rock with HCl	28	1950-1969
1170	Phosphate Rock-Calcination	59	Compiled 1975
1172	Beneficiation of Phosphate Ores	176	1949-1975
1178	Sequestering Fe & Al Impurities in Phosphoric Acid and Ammoniated Phosphates	11	1954-1973
1186	A Bibliography on Citrate-Insoluble P_2PO_5	26	1935-1969
1193	Gel Permeation Chromatography of Phosphorus Compounds	5	1966-1969
1194	Ammonium Phosphate from Wet-Process Phosphoric Acid	111	1959-1975
1215	Monoammonium Phosphate	154	Compiled 1973
1237	Calcium Phosphates--Citrate Solubility	5	1962-1970
1240	Alternate Methods of Phosphorus Production	27	1948-1970
1247	Urea Phosphate	120	1923-1975
1254	Oxidation of Phosphorous Acid	22	1909-1974
1271	Manufacture of Sodium Tripolyphosphate	36	1947-1973
1280	DAP/TSP Comparison	19	1960-1974
1281	Extraction of Uranium from Phosphate Rock and Phosphoric Acid	119	1948-1974
1282	Treatment & Recovery of Waste Products (Fluorine and Gypsum) from Wet-Process Phosphate Acid Manufacture	144	1961-1974
1299	Oxyapatites	7	1960-1971
1361	Removal of Magnesium from Phosphate Rock and Phosphorus Compounds	14	1962-1973
1363	Metal Ammonium Phosphates	60	Compiled 1973
1374	Solvent Extraction of Phosphoric Acid	36	1959-1972
1375	Superphosphoric Acid	50	1958-1971
1379	Wet Process Phosphoric Acid: Manufacturing Technology. Production Economics.	154	1967-1973
1379 Suppl.	Wet Process Phosphoric Acid: Manufacturing Technology. Production Economics.	20	Compiled 1976
1384	Production of Elemental Phosphorus	117	1938-1973
1405	Phosphorous Acid and Its Compounds	8	1957-1974
1410	Urea-Ammonium Phosphate	38	1960-1975
1414	Solubility Relationships in Metal-Phosphate Systems	75	1968-1974
1427	Manufacture of Triple Superphosphate	69	1949-1974
1437	Flotation Agents for Phosphates	122	1957-1975
1438	Antifoam Agents for Wet Phosphoric Acid Manufacture	15	1957-1974
1461	Electrostatic Beneficiation of Phosphate Rock	13	1961-1973
1470	Granulation of Phosphate Rock for Direct Application	20	1961-1974
1481	Magnesium Phosphate Fertilizers: Manufacture & Use	150	1950-1975
1493	Wet Process Phosphoric Acid Production: Air/Water Pollution Rules, Regulations, Treatment Facilities	35	1960-1975

Number	Subject	No. of Refs.	Period
	IIB. Potassium Compounds		
1314	Manufacture of Potassium Sulfate from Potassium Chloride and Sulfuric Acid	14	Compiled 1972
1365	Potassium Hydroxide in Liquid Fertilizers	21	1957-1973
1373	Manufacture of Potassium Fertilizers	83	1968-1973
1388	Potassium Chlorate Manufacture from Potassium Chloride	9	1907-1973
1474	Potassium Chloride from Carnallite	19	1959-1975
1476	Mining and Beneficiation of Potash	81	1965-1975
	IIC. Nitrogen Compounds (See also 1019, 1023, 1067, 1127, 1159, 1194, 1317, 1363, 1410)		
1052	Corrosion of Nitrogen Fertilizer Solutions	112	1958-1973
1053	Ammonia Production	288	1951-1975
1057	A Basic Booklist on Production of Ammonia, Ammonium Nitrate, Nitric Acid and Urea	34	1947-1973
1074	Recovery of Plantinum from Ammonia-Oxidation Catalysts	10	1956-1967
1100	Ammonium Nitrate: Hygroscopicity	31	1958-1969
1104	Conditioning Urea	68	1957-1973
1111	Granulation from Melts: Urea and Ammonium Nitrate	79	1926-1969
1115	Concentrated Nitric Acid Production Processes	77	1963-1971
1129	Production Processes for Potassium Nitrate	58	1950-1970
1161	Ammonium Nitrate-Ammonium Sulfate	44	1921-1970
1167	Adding MgO to NH_4NO_3	7	1958-1970
1169	Electrolytic Hydrogen in Ammonia Production	22	Compiled 1973
1215	Monoammonium Phosphate	154	Compiled 1973
1239	Urea Solutions Production and Transportation	8	1964-1970
1247	Urea Phosphate	116	1923-1975
1262	Manufacture of Ammonium Nitrate Prills	28	Compiled 1972
1286	Non-Agricultural Uses of Ammonia	161	Compiled 1973
1301	Urea Prilling	32	1956-1974
1305	Urea Synthesis: Physical, Chemical, and Thermodynamic Properties	69	1950-1973
1310	Urea-Calcium Nitrate: Hygroscopicity	6	Compiled 1972
1317	Manufacture of Ammonium Sulfate	65	Compiled 1974
1322	Urea-Ammonium Nitrate Solutions	23	1907-1972
1324	Urease and Urease Activity	839	1900-1973
1324 Suppl.	Urease and Urease Activity Supplement	67	Compiled 1974
1325	Sulfur Coated Urea - Production and Use	55	1947-1974
1326	Corrosion of Urea Solutions	17	1964-1972
1333	Properties and Structure of Guanidine and Triuret	10	Compiled 1972
1337	Reactions of Ammonia and Sulfur Dioxide	21	Compiled 1972
1338	Removal of CO_2 from Gas for Ammonia Synthesis	75	Compiled 1975
1339	Manufacture of Ammonium Sulfate from Sodium Sulfate	29	Compiled 1973
1345	Ureaform - Manufacture and Properties	108	Compiled 1973
1347	Oxamide	22	Compiled 1973
1348	CDU and FLORANID	14	Compiled 1973
1349	Urea-Z (Urea Acetaldehyde)	12	Compiled 1973
1350	Miscellaneous Urea-Based Slow Release Fertilizer	20	Compiled 1973
1351	IBDU	28	Compiled 1973

IIC. Nitrogen Compounds (Continued)

Number	Subject	No. of Refs.	Period
1376	Calcium Cyanamide in Agriculture	73	1957-1972
1378	Ammonium Thiosulfate	15	Compiled 1973
1391	Urea Production	237	1950-1973
1397	Ammonia and Fertilizers from Coal	110	1957-1975
1409	Calcium Ammonium Nitrate	84	1957-1974
1412	Formamide Use in Fertilizers	9	1950-1974
1425	Urea Manufacture--Hydrolysis	17	1957-1974
1430	Urea Granulation	37	Compiled 1974
1444	Waste Water from Urea Plants	13	1966-1974
1450	Compound Fertilizers Made With Urea	80	1962-1974
1479	Chemical Nitrogen Fixation at Moderate Temperature & Pressure	91	Compiled 1975
1495	Ammonium Nitrate: Crystal Structure & Phase Transformations	60	1960-1975

IID. Micronutrients

(See also 1015)

1040	Incorporation of Micronutrients into Solid Fertilizers	64	1960-1973
1058	Addition of Micronutrients to Liquid Fertilizers	88	1958-1973
1167	Adding MgO to NH_4NO_3	7	1958-1970
1183	Fluorides in Fertilizers	22	1950-1969
1184	Fluorine in Plants: Analytical Methods	7	1953-1966
1206	Mercury in Plants and Soils	115	Compiled 1970
1232	Manufacture of Boron Fertilizer	17	1956-1970
1252	Zinc Coatings on Granular Fertilizer	11	1959-1970
1378	Ammonium Thiosulfate	15	Compiled 1973

IIE. Coatings

(See also 1104)

1011	Coatings for Slow-Release Fertilizers	128	Compiled 1972
1012	Coatings to Prevent Caking	48	1964-1970
1015	Coatings as Carriers for Micronutrients	7	1965-1969
1241	Urea-Formaldehyde as a Fertilizer Coating Agent	9	1959-1970
1252	Zinc Coatings on Granular Fertilizer	11	1959-1970
1303	Coatings for Dust Control in Granulated Fertilizers	16	Compiled 1972
1325	Sulfur Coated Urea-Production and Use	55	1947-1974

IIF. Plants and Equipment

(See also 1052, 1075, and 1076)

1051	Maintenance for Production Plants	29	1964-1970
1075	Materials of Construction in Urea Plants	18	1960-1970
1076	Nitric Acid: Materials of Construction	16	1958-1967
1080	Pilot Plants	40	1964-1969
1107	Corrosion in Manufacture of Fertilizer Chemicals	26	1965-1969
1158	Conveyors	81	1965-1971
1182	Chemical Plant Start-Up	20	1953-1970
1221	Pumps for Suspension	23	1962-1970
1224	Cooling Towers: Design and Performance	154	1961-1970
1266	Corrosion and Water Treatment	46	Compiled 1971
1313	Quality Control in the Chemical Plant	52	1956-1972
1318	The Oslo-"Krystal" Crystallizer	8	Compiled 1972

IIG. Sulfur and Sulfur Compounds

Number	Subject	No. of Refs.	Period
1043	Recovery of Sulfur, Ammonium Sulfate, and Sulfuric Acid from Gypsum	42	Compiled 1972
1164	Bacteriological Digestion of Gypsum as a Source for Sulfur	13	1931-1969
1225	Reactions of SO_2 and Magnesium Oxide	44	1948-1970
1226	Physical Properties of $MgSO_3$	28	Compiled 1970
1230	Corrosion by Magnesium Sulfite	2	1952-1959
1236	Sulfur-Containing Fertilizers	281	1960-1973
1250	Technology of Sulfuric Acid Manufacture-Contact Process	282	1950-1971
1260	Sulfur/Sulfuric Acid: Production, Consumption and Marketing in U. S.	59	1970-1975
1311	Market Potential for Gypsum	8	Compiled 1972
1317	Manufacture of Ammonium Sulfate	205	1947-1972
1317 Suppl.	Manufacture of Ammonium Sulfate	65	Compiled 1974
1372	Uses of Gypsum and Sodium Sulfate	58	Compiled 1973
1423	Sulfuric Acid Manufacturing Technology	35	1970-1974
1424	Prilling Sulfur	18	Compiled 1974
1449	Granulation of Gypsum	12	1965-1975
1497	Oxidation of Ammonium Sulfite	17	1963-1975

III. APPLICATION METHODS AND EQUIPMENT

1025	Injection Application of Anydrous Ammonia	19	1957-1968
1082	Foliar Application of Fertilizers	144	1953-1970
1090	Aerial Application of Pesticides	67	1960-1973
1110	Pop-Up Fertilizers	13	1966-1969
1207	Foliar Application of Ammonium Nitrate Fertilizer	29	Compiled 1970
1243	Fertilizer Placement for Potatoes (Row vs. Broadcast)	28	Compiled 1971
1244	Fertilizer Placement for Tomatoes (Row vs. Broadcast)	13	Compiled 1971
1246	Foliar Application of Fertilizer on Jute	4	1959-1970
1287	Nonuniform Application of Fertilizers (Causes, Corrections, Effects)	34	1962-1973
1288	Fertilizer Application Equipment (General, Solid, Aerial, Liquid)	222	1960-1971
1315	Foliar Application of Phosphates	44	1953-1972
1319	N Fertilizer Applied in Irrigation Water	37	1934-1974
1446	Band vs. Broadcast Placement of Phosphate Fertilizer for Maize, Sorghum, and Soybeans	35	1956-1974

IV. STORAGE AND TRANSPORTATION

1009	Ammonia Pipeline	36	1967-1970
1010	Storage of Fertilizers	86	Compiled 1973
1014	Phosphoric Acid: Storage, Transportation, Corrosion,	78	Compiled 1974
1050	Liquid Fertilizer Storage and Transportation	41	Compiled 1973
1060	Transportation and Handling of Molten Sulfur	18	1959-1974
1105	Storage and Transportation of Urea	13	1961-1973
1158A	Conveying Fertilizer Bags	14	Compiled 1971
1175	Fertilizer Ships and Shipping	37	Compiled 1973
1220	Fertilizer Bags and Bagging	37	1961-1973
1239	Urea Solutions Production and Transportation	8	1964-1970

Number	Subject	No. of Refs.	Period
	V. POLLUTION		
1013	Air Pollution: Nitrogen Oxides - Toxicity & Control	61	1966-1970
1028	Scrubber for Chemical Plants	41	1967-1970
1042	Pollution from Fertilizer Manufacturing Plants	72	1964-1970
1061	Effects of Atmospheric Fluorides on Plants and Animals	169	1950-1974
1081	Nitrate Toxicity	105	1939-1968
1088	Effect of Elemental Phosphorus, P_2O_5, Fluoride, and Particulate Matter on Fish and Marine Life	49	1958-1972
1118	Recovery of Ammonia from Waste Gases	17	1936-1962
1123	Neutralization of Sulfuric and Chromic Acid Wastes	27	1949-1967
1171	Environmental Pollution Sources	33	1967-1969
1173	Incineration of Sludges	34	1959-1969
1206	Mercury in Plants and Soils	115	Compiled 1970
1208	Mercury in Aquatic Environment	96	1927-1970
1225	Magnesium Oxide Used in Sulfur Dioxide Scrubbing (Excluding Dolomite)	44	1948-1970
1233A	Wet Scrubbing - Dust	318	1930-1970
1233B	Wet Scrubbing - Sulfur Dioxide	281	1930-1970
1294	Effects of Air Pollution on Lichens and Bryophytes	33	1940-1974
1307	Damage to Vegetation in the Copper Basin in Tennessee	19	Compiled 1972
1337	Reactions of Ammonia and Sulfur Dioxide	21	Compiled 1972
1340	Recovery of Fluorine from Phosphate Plant Stack Gases	46	Compiled 1973
1356	Potassium Carbonate Method for Removal of H_2S from Gases	28	1958-1973
1364	Thermal Pollution Research	90	1970-1973
1367	Cadmium Pollution	62	Compiled 1973
1389	Heavy Metals in Sewage Sludge and Organic Waste	62	1961-1973
1407	Nickel in Plants, Soils, and Surface Water	90	1959-1974
1411	Phosphorus Removal from Waste Water	160	1967-1974
1416	Sulfur Dioxide Effects on Plants and Animals	169	1967-1974
1419	Dechlorination of Water	7	Compiled 1974
1439	Selected References on Refuse Incineration	111	1969-1974
1443	Ammonia Removal from Waste Waters	83	1966-1974
1444	Waste Water from Urea Plants	13	1966-1974
1454	Effects of Acrolein in Aquatic Ecosystems	17	1959-1971
1455	Published Reports of U.S. Government Sponsored Research on Topics Relating to Agriculture and the Environment	31	1972-1974
1480	Flue Gas Desulfurization by Fluidized-Bed Combustion	34	1969-1975
1488	Nitrate Leaching	170	1971-1975
1493	Wet Process Phosphoric Acid Production: Air/Water Pollution Rules, Regulations, Treatment Facilities	35	1960-1975
	VI. MARKETING		
1031	Marketing Fertilizers	208	Compiled 1975
1078	Merchant Credit in the Fertilizer Industry	13	1963-1969
1114	Experiences in Fertilizer Market Development	42	1955-1969
1195	Fertilizer Economics (Nine Selected Bibliographies)		
	#1 (Rev.) - Books on Fertilizer Economics (TVA TL)	22	Compiled 1974
	#2 - Costs of Producing Fertilizers	90	1965-1972
	#3 (Rev.) - Costs of Marketing Fertilizer	38	1965-1974
	#4 - Inventory Control	3	1965-1972
	#5 - Costs of Transporting Fertilizers	24	Compiled 197
	#6 (Rev.) - Pricing Practices in the Fertilizer Industry	90	1965-1974
	#7 (Rev.) - Supply-Demand Studies	206	1970-1974
	#8 (Rev.) - Governmental Policies and Regulations of the Fertilizer Industry	45	1966-1974
	#9 - Farmers' Attitudes Towards Fertilizer Use	19	1954-1972

VI. MARKETING (Continued)

Number	Subject	No. of Refs.	Period
1366	Fertilizer Demand Analysis	15	Compiled 1973
1382	Books on Marketing (Found in MSTL)	47	Compiled 1973
1490	Fertilizer Dealer Services	85	1958-1976

VII. ORGANIC MATERIALS

Number	Subject	No. of Refs.	Period
1091	Humates - Humic Acid - Fluvic Acid	99	1959-1969
1092	Bone for Fertilizer and Animal Feed	39	1951-1975
1093	Guano as Fertilizer	52	Compiled 1975
1098	Compost (Fertilizers and Soil Amendments) from Town Refuse	300	1958-1973
1108	Milorganite	13	1928-1963
1205	Leather as Fertilizer	17	Compiled 1975
1223	Organic Fertilizers	22	1954-1970
1238	Bark as Soil Amendment	38	1959-1970
1265	Effect of Crop Residue on Soil Fertility and Crop Yields	105	1960-1970
1272	Fish and Fish Meal as Fertilizers	35	1950-1971
1304	Paper Mill Waste as Fertilizer Soil Amendment	13	1962-1972
1327	Ammelide and Ammeline: Analysis and Manufacture	17	1937-1971
1389	Heavy Metals in Sewage Sludge and Organic Waste	62	1961-1973
1429	Peat (Formation, Transformation, and Chemical Composition)	43	Compiled 1974

VIII. PESTICIDES

Number	Subject	No. of Refs.	Period
1056	Pesticide Manufacture and Use: A Basic Booklist	33	1955-1971
1090	Aerial Application of Pesticides	67	1960-1973
1097	Herbicides and Pesticides in Liquid Fertilizers	99	Compiled 1973
1130	Pre-Emergence Herbicides in Relation to Temperature and Moisture	20	1951-1967
1203	Insecticides-Herbicides, Sugar Industry in South America	37	1967-1970
1242	Movement of Herbicides and Pesticides	70	1960-1970
1278	Pesticides in Granular Fertilizers	32	Compiled 1972
1295	Soybean Cyst Nematodes	64	1962-1972
1491	Economic Impact of Pesticide Bans	53	1971-1976

IX. PLANT NUTRITION

Number	Subject	No. of Refs.	Period
1032	Cation Exchange Capacity of Plant Roots	23	1947-1969
1189	Effect of Soil Profile Properties on Plant Response	28	1965-1970
1191	Effect of Moisture Supply in Soil on Crop Response to Fertilizer	51	1965-1970
1257	Fertilizer Trials in High pH Soils	85	Compiled 1971
1265	Effect of Crop Residue on Soil Fertility and Crop Yields	105	1960-1970
1279	Plant Analysis as a Guide for Fertilizer Recommendations	101	1953-1971
1289	Agricultural Chemicals and Food Quality	29	Selected Refs.
1370	Influence of Roots on Nutrient Uptake	144	1969-1973
1371	The Application of Growth Regulators to Plants	70	Compiled 1973
1380	Effects of Soil Temperature on Nutrient Uptake and Plant Growth	166	1960-1973

Number	Subject	No. of Refs.	Period
	IXA. Nitrogen		
1001	Ammoniated Phosphates - Manufacture, Patents & Use	284	Compiled 1973
1021	Use of Anhydrous and Aqueous Ammonia	167	1951-1975
1022	Biuret in Fertilizers and Feeds	226	Compiled 1975
1023	Nitric Phosphates: Manufacture and Use	237	1951-1975
1033	Nitrogen Nutrition of Mycorrhizal Fungi	14	1952-1969
1035	Nitrate Reductase Activity in Higher Plants	14	1951-1967
1067	Ammonium Polyphosphates	137	1952-1972
1069	Foliar Application of Urea on Non-Cereal Crops	48	1958-1968
1070	Use of Urea Solutions on Cereal Crops	29	1958-1967
1087	Urea-Formaldehyde Fertilizer: Agronomic Aspects	85	1958-1968
1103	Use of Fluid Nitrogen Fertilizers	106	1951-1973
1122	Ammonium Thiocyanate in Agriculture	15	1946-1965
1146	Nitrogen Mineralization	16	1927-1965
1154	Comparison of Urea and Ammonium Nitrate for Effectiveness as Nitrogen Fertilizer	34	1957-1970
1202	Relative Effectiveness of NO_3-Nitrogen and NH_4-Nitrogen on Crops other than Paddy	57	1960-1970
1207	Foliar Application of Ammonium Nitrate Fertilizer	29	Compiled 1970
1210	Urea Transformations in Waterlogged Soils	19	1945-1970
1325	Sulfur Coated Urea - Production and Use	55	1947-1974
1329	Urea Hydrolysis Under Field Conditions	77	1962-1974
1330	Glycoluril as a Slow-Release Fertilizer	8	Compiled 1972
1406	Ammonium Bicarbonate as Fertilizer	22	1948-1970
1409	Calcium Ammonium Nitrate	84	1957-1974
1422	Azotobacter Cultures as Fertilizer	28	Compiled 1974
1448	Effects of Hydrazine on Plants and Soil Microorganisms	11	1947-1966
1458	Use of Ammonium Chloride as a Fertilizer	34	1957-1974
1462	Nitrogen Fertilizers for Rice	122	1972-1975
1496	Ammonium Sulfate in Plants & Soils	81	1965-1975
	IXB. Phosphorus and Potassium		
1037	Basic Slag	132	Compiled 1975
1046	Agronomic Effects of Potassium Pyrophosphates	12	Compiled 1972
1067	Ammonium Polyphosphates	137	1952-1972
1101	Potassium Phosphate Fertilizers	84	1936-1971
1109	Phosphate Rock as Fertilizer	99	1934-1970
1109 Suppl.	Phosphate Rock as Fertilizer	28	Compiled 1974
1188	Potassium-Magnesium Relationships in Plant Nutrition	25	1965-1970
1190	Effect of Time of Application of Potassium Fertilizers on Plant Response	22	1965-1971
1211	Crop Response to Polyphosphate Fertilizers	29	1958-1970
1255	Agronomic Effects of Calcium Metaphosphates	30	Compiled 1971
1396	Agricultural Uses of Flue Dust from Portland Cement Manufacture	59	1907-1973
1410	Urea-Ammonium Phosphate	38	1960-1975
1417	Comparative Studies of Potassium Fertilizers	28	1968-1973
1463	Phosphorus-Zinc Interactions	84	1968-1974
1467	Utilization of Phosphogypsum	68	1963-1975
1468	Use of Rhenania Phosphate	27	1953-1974
1478	Phosphorus Nutrition of Alfalfa, Blue Grass Clover, Orchard Grass, Reed Canary Grass, & Rye Grass	332	1950-1974
1481	Magnesium Phosphate Fertilizers: Manufacture & Use	150	1950-1975
1487	Bacterial Phosphate Fertilizers	62	1962-1976

Number	Subject	No. of Refs.	Period
	IXC. Sulfur		
1026	Agronomic Effects of Sulfur	57	1941-1967
1112	Agricultural Use of Gypsum	43	1954-1967
1122	Ammonium Thiocyanate in Agriculture	15	1946-1965
1496	Ammonium Sulfate in Plants & Soils	81	1965-1975
	IXD. Other Secondary and Minor Elements		
1041	Crop Response to Micronutrients	285	1963-1970
1079	Magnesium in Agriculture	117	1964-1970
1083	Iron in Plant Nutrition	114	1932-1971
1177	Zinc Nutrition of Sugar Beets	46	1950-1969
1181	Chromium Nutrition of Plants and Animals	88	1941-1970
1185	Effects of Root-Absorbed Fluorides on Plants	36	1949-1969
1188	Potassium-Magnesium Relationships in Plant Nutrition	25	1965-1970
1231	Boron Deficiency and Toxicity	112	1961-1970
1256	Manganese in Plant Nutrition	197	Compiled 1971
1267	Agronomic Use of Fritted Trace Elements	28	Compiled 1971
1270	Agricultural Use of Limestone	26	1965-1971
1334	Agronomic Effects of Fluorine in Fertilizers	15	Compiled 1972
1360	Fluorine Reactions in Soils and F Uptake by Plants	29	Compiled 1973
1386	Arsenic in Fertilizers, Soils, and Plant Nutrition	50	1950-1973
1387	Cobalt in Plant Nutrition	103	1957-1973
1404	Magnesium Oxide in Fertilizers and Feed	25	1967-1973
1456	Selected References on Secondary and Trace Elements in Agriculture	98	1969-1973
1463	Phosphorus-Zinc Interactions	84	1968-1974
1465	Carbon Dioxide as Fertilizer	39	1957-1974
	IXE. Effects of Time and Method of Application		
1082	Foliar Application of Fertilizers	144	1951-1970
1110	Pop-Up Fertilizers	13	1966-1969
1152	Leaf Damage from Liquid Fertilizer	20	1950-1969
1179	Winter Application of Fertilizers	28	1931-1971
1187	Residual Effects of Fertilizers and Manures on Subsequent Crops	47	1965-1970
1190	Effect of Time of Application of Potassium Fertilizers on Plant Response	22	1965-1971
1192	Effect of Fertilizer Placement on Crop Response to Fertilizer	86	1965-1970
1199	Crop Response to Blended vs. Compounded Fertilizers	15	Compiled 1970
1269	Effect of Fertilizers on Seed Germination	27	1961-1971
1319	N Fertilizer Applied in Irrigation Water	37	1934-1974
	IXF. Plant Analysis		
1096	Plant Tissue Analysis	30	1958-1968
1279	Plant Analysis as a Guide for Fertilizer Recommendations	101	1953-1971
1393	Sample Preparation for Nitrate Analysis: Effects of Drying	12	1958-1973
1399	Foliar Analysis of Pine	38	1954-1974

X. PLANT NUTRITION--SPECIFIC CROPS

Number	Subject	No. of Refs.	Period
1048	Effect of Fertilizer Nutrients on Nicotine Content of Tobacco	18	1955-1965
1094	Fertilizers for Tea and Coffee	107	1959-1970
1099	Boron: Effect on Trees and Seedlings	106	1954-1969
1121	Potassium Nutrition of Landscape Plants	46	Compiled 1972
1132	Nitrogen Uptake by Coniferous Plants	15	1958-1966
1138	Fertilizers for Pineapples	101	1932-1970
1139	Fertilizers for Rice, Sugarcane, Bananas, Corn, Cotton and Sesame	156	1950-1970
1149	Forest Fertilization	18	1938-1966
1177	Zinc Nutrition of Sugar Beets	46	1950-1969
1196	The Effect of Fertilizers (N, P, K) on Fungal Diseases of Forest Trees	46	1953-1969
1197	The Nitrogen Cycle in Forest Ecosystems	239	1956-1969
1198	Nutrition of Rice	72	1963-1970
1200	Foliar Analysis of Rubber Plant	70	1955-1970
1201	Selected References on Pecan Culture	82	Compiled 1970
1217	Micronutrient Nutrition of Wheat	39	1964-1970
1218	Mineral Nutrition of Peas and Beans	56	1965-1970
1222	Utilization of Phosphorus Applied to Alfalfa	124	Compiled 1970
1229	Fertilization of Sorghum	47	1956-1970
1234	Application of Micronutrients to Grasses	25	1957-1971
1259	Fertilization of Tropical Pastures	147	1970-1971
1268	Trace Element Fertilization in Pastures	171	Compiled 1971
1273	Fertilizers for Bananas	79	1962-1971
1275	Winter Hardiness of Forage as Affected by Fertilizer	39	1945-1971
1284	Soil Analysis and Tomato Production	17	1960-1970
1285	Foliar Applied Micronutrients for Tomatoes	10	1960-1970
1290	Slow-Release N & Nitrification Inhibitors in Rice Culture	113	1954-1972
1297	Nitrogen Fertilization of Soybeans	49	1959-1971
1298	Nitrogen Fertilization of Alfalfa and Alfalfa-Grass	61	1960-1972
1300	Fertilizers for Coconuts	48	1967-1971
1316	Preparation of Tomato Seedlings	47	1962-1972
1321	Citrus Horticulture in North and South America	79	Compiled 1972
1332	Grape Culture	119	Compiled 1972
1352	Nitrogen Nutrition of Cotton	111	1960-1972
1354	Millet; Fertilization and Yield	99	Compiled 1973
1381	Soybean Production (Selected References)	87	1968-1973
1420	Fertilizing Eucalyptus	20	Compiled 1974
1421	Fertilization of Pine Trees	123	Compiled 1974
1445	Use of Sulfur-Coated Urea on Forage Plants	35	1970-1974
1451	Fertilizers for Strawberries	57	1967-1974
1452	Fertilizers for Oil Palms	65	1967-1974
1453	Fertilisers for Rubber Trees	29	1967-1975
1472	Hops - Cultivation and Fertilization	37	1960-1975
1473	Tall Fescue Fertilization	103	1960-1975
1475	Mycorrhizal Effects on Nutrient Uptake by Plants	141	1945-1975
1483	American Holly (*Ilex opaca*)	40	1951-1974
1484	Franklinia alatamaha	14	1943-1976
1486	Rice Varieties Response to Phosphate Fertilization	54	1972-1975

Number	Subject	No. of Refs.	Period
	XI. SOIL-NUTRIENT RELATIONSHIPS		
1146	Nitrogen Mineralization	16	1927-1965
1210	Urea Transformations in Waterlogged Soils	19	1945-1970
1329	Urea Transformations in Soil	77	1958-1973
1385	Soil Water Measurement	144	1965-1973
1390	Denitrification	224	1920-1973
1394	Nitrification Inhibitors	178	1968-1973
1395	Soil Nitrogen Analysis for Fertilizer Recommendations	62	1948-1973
1431	Amorphous Matter in Soils (Particularly Tropical Soils)	48	Compiled 1974
1432	Classification of Soils (Particularly Tropical Soils)	81	Compiled 1974
1434	Tin in Soils	37	Compiled 1974
1488	Nitrate Leaching	170	1971-1975
1489	Soil Water Movement	142	1970-1975
	XII. ANIMAL FEEDS		
1022	Biuret in Fertilizers and Feeds	225	Compiled 1975
1064	Feed-Grade Phosphates Manufacture	76	1957-1975
1065	Feed-Grade Phosphates: Evaluation of Use	90	1957-1975
1095	Preparation of Animal Feed Supplements by Defluorination of Phosphate Rock--With Special Reference to Removal of Fe and Al_2O_3	24	1956-1965
1125	Urea as a Feeding Stuff	46	1961-1968
1216	Inorganic Preservation Additives for Corn and Silage	17	1963-1970
1312	The Effect of Temperature and Humidity on Growth and Feed Conversion Efficiency of Poultry, Cattle and Service	97	Compiled 1972
1358	Ammoniated Molasses as Animal Feed	18	1937-1973
1359	Wood and Wood Products for Cattle Feed	32	Compiled 1973
1404	Magnesium Oxide in Fertilizers and Feed	25	1967-1973
1413	Use of Slow-Release Nitrogen Compounds in Animal Feeds	15	1965-1973
	XIII. DEVELOPING COUNTRIES		
1072	Iran	30	Compiled 1968
1077	Pakistan	59	Compiled 1968
1084	Chile	30	Compiled 1968
1102	Agronomic and Economic Benefits of Fertilizer Application to Grain Crops in India	37	1955-1969
1106	Bolivia	56	Compiled 1969
1133	Mexico	44	Compiled 1968
1134	India	97	Compiled 1968
1142	Agriculture in Indonesia	73	1949-1969
1151	Fertilizer Marketing and Distribution in India	31	1966-1969
1153	Brazil	113	1955-1969
1165	The Fertilizer Industry in the Republic of South Africa	17	1957-1969
1209	Paraguay	15	Compiled 1970
1212	Trinidad and Tobago	40	Compiled 1970
1227	Fertilizers: Tropical Africa	85	1962-1970
1228	Philippines	62	1965-1973
1235	Vietnam	25	Compiled 1971
1253	Establishing a Business in Pakistan	15	Compiled 1971

XIII. DEVELOPING COUNTRIES (Continued)

Number	Subject	No. of Refs.	Period
1261	Fertilizer Production and Technology in the U.S.S.R.	49	1969-1971
1274	Fertilizer Production and Use in Guatemala	25	1964-1971
1277	Morocco: Fertilization - Irrigation	40	1960-1971
1291	Ghana	19	1959-1972
1292	Taiwan (Publications in the MSTL)	32	Compiled 1972
1320	Venezuela	41	Compiled 1975
1328	Spain	17	Compiled 1972
1369	Central America (Costa Rica, El Salvador, Guatemala, Honduras and Nicaragua)	70	Compiled 1973
1377	Romania	20	Compiled 1973
1415	Geology of Niger	24	1907-1973
1435	Colombia	69	Compiled 1974
1441	The Republic of Zaire	23	Compiled 1975
1447	Dominican Republic	44	Compiled 1975
1459	Agriculture in New Guinea	19	1965-1974
1471	Egypt - Fertilizer Industry and Use	35	1967-1975
1494	Role of Agricultural Consultants	25	1965-1975

XIV. FUEL SOURCES AND PROCESSES

Number	Subject	No. of Refs.	Period
1323	Coal Mine Strip Areas Reclamation	95	1966-1975
1341	Current Biological and Ecological Studies Done in the Vicinity of Deep or Strip Mines	31	Compiled 1973
1383	Coal Gasification	333	1947-1973
1383 Suppl.	Koppers-Totzek Articles and Patents	32	1947-1973
1400	Liquefaction of Coal	68	1959-1974
1402	Selected Processes for Removal and/or Recovery of S Compounds from Fuel Gases	53	1955-1974
1403	Methane Production from Organic Wastes	28	1947-1973
1439	Selected References on Refuse Incineration	111	1969-1974

XV. MISCELLANEOUS

Number	Subject	No. of Refs.	Period
1006	Phosphate Fire Retardants: Composition, Application, and After Effects	28	1961-1973
1008	Sub-Irrigation	16	1966-1970
1066	Ammonia Cells	20	1961-1967
1073	Erosion in Urban-Suburban Areas	14	1963-1968
1086	Manufacture of Hydrogen Fluoride from Fluorosilicic Acid	18	1961-1966
1116	Reduction of Alumina	32	1962-1968
1126	Manganese Deficient Areas of the World	72	1933-1965
1136	Cavitation in Liquids	28	1949-1966
1141	Manufacture of Formic Acid (Sodium Formate Process)	12	1935-1966
1155	Alfalfa Cutting Management	91	1959-1969
1166	Books about TVA	16	1952-1969
1168	High Yielding Cereal Varieties	162	1962-1969
1204	Geology of the Tennessee Valley Region	62	Compiled 1970
1245	Bioelectricity	40	1966-1970
1248	Gypsum Wallboard Manufacture	44	1960-1970
1251	Food Preference and Their Nutritive Value for Wildlife in the Tennessee Valley	33	Compiled 1971
1258	Trout Farming	16	1960-1970
1263	Magnesia-Base Sulfite Pulping	108	1907-1971
1264	Metric System (Selected References)	19	Compiled 1971

XV. MISCELLANEOUS (Continued)

Number	Subject	No. of Refs.	Period
1293	Impact Effects of Materials and Structures	56	Compiled 1972
1302	pH and/or S Content of Precipitation (Meteorology)	42	1916-1972
1306	Pumped Storage for Hydroelectric Power	--	1928-1972
1308	Selected References on the Activation of Clay with Acids and the Recovery of Aluminum	32	1940-1972
1309	Nitrogen Fixation in the Phyllosphere	11	1956-1971
1335	Handling and Use of NH_4NO_3 as an Explosive	40	1970-1972
1336	Selected References on Varied Applications of Spectral Analysis	39	Compiled 1972
1342	Cabomba	19	Compiled 1973
1343	The Importance of Integrity in Leadership, Management and Supervision	26	Compiled 1973
1344	Nelumbo	145	Compiled 1973
1353	Agricultural Policy in the United States	21	Compiled 1973
1357	Pulse Polarography	19	1960-1973
1362	Preparation of Nonconducting Samples for SEM	8	Compiled 1973
1398	Electroless Plating	42	1969-1973
1401	Absorption of Nitrogen Oxides by Water and Nitric Acid Solutions	21	1920-1972
1408	Vaterite	40	1924-1973
1426	Toxicity of Polyethylene	15	1967-1973
1436	Movement of Radionucleotides and Radionuclides into Food Chains	63	Compiled 1975
1440	Mollusks - Freshwater and Estuarine	158	Compiled 1974
1440 Suppl.	Mollusks - Freshwater and Estuarine	122	Compiled 1975
1457	Effect of Climatic Change on Food Supply	15	1973-1975
1460	Vertical Integration: Applications in Various Industries	30	1965-1975
1464	Drifting Organisms in Streams	44	1965-1975
1466	Elemental Phosphorus Poisoning	39	1957-1974
1482	Lithium-Drifted Germanium Radiation Detectors	168	1971-1975
1485	Mathematical Methods for Gain Compensation in NaI Gamma-Ray Scintillation Spectra	25	Compiled 1976

April 27, 1976